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How to Add a Five-Membered Ring to Polycyclic Aromatic Hydrocarbons (PAHs) – Molecular Mass Growth of the 2-Naphthyl Radical ($C_{10}H_7$) to Benzindenes ($C_{13}H_{10}$) as a Case Study

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ABSTRACT

The three-ring polycyclic aromatic hydrocarbons (PAHs) 3*H*-benz[*e*]indene ($C_{13}H_{10}$) and 1*H*-benz[*f*]indene ($C_{13}H_{10}$) along with their naphthalene-based isomers 2-(prop-2-yn-1-yl)naphthalene ($C_{13}H_{10}$), 2-(prop-1-yn-1-yl)naphthalene ($C_{13}H_{10}$), and 2-(propa-1,2-dien-1-yl)naphthalene ($C_{13}H_{10}$) were formed through a "directed synthesis" via a high temperature chemical micro reactor under combustion-like conditions (1300 ± 35 K) through the reactions of the 2-naphthyl isomer ($C_{10}H_7^{\bullet}$) with allene (C_3H_4) and methylacetylene (C_3H_4). The isomer distributions were probed utilizing tunable vacuum ultraviolet radiation from the Advanced Light Source (ALS) by recording the photoionization efficiency curves at mass-to-charge of m/z = 166 ($C_{13}H_{10}$) and 167 ($^{13}CC_{12}H_{10}$) of the products in a supersonic molecular beam. Complemented by electronic structure calculations, our study reveals critical mass growth processes via annulation of a five-membered ring from the reaction between aryl radicals and distinct C_3H_4 isomers at elevated temperatures as present in combustion processes and in circumstellar envelopes of carbon stars. The underlying reaction mechanisms proceed through the initial addition of the 2-naphthyl radical with its radical center to the π-electron density of the allene and methylacetylene reactants via entrance barriers between 8 and 14 kJ mol^{-1}, followed by isomerization (hydrogen shifts, ring closure), and termination via atomic hydrogen losses accompanied by aromatization. The reaction mechanisms reflect the formation of indene – the prototype PAH carrying a single five- and a single six-membered ring – synthesized through the reaction of the phenyl radical ($C_6H_5^{\bullet}$) with allene and methylacetylene. This leads us to predict that aryl radicals – upon reaction with allene/methylacetylene – may undergo molecular mass growth processes via ring annulation and de-facto addition of a five-membered ring to form molecular building blocks essential to transit planar PAHs out of the plane.

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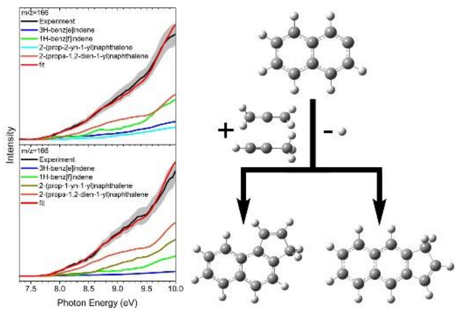

The reaction of aryl radicals with allene/methylacetylene leads to five-membered ring addition in PAH growth processes.

1. Introduction

Molecular beam experiments with crossed beams[1-5] and pyrolytic micro reactors[6-9] critically aid in fundamental understanding of the formation mechanisms of polycyclic aromatic hydrocarbons (PAHs)[10-24] along with their methylated counterparts carrying up to four six-membered rings. They have provided profound insight of complementary hydrogen abstraction – acetylene addition (HACA)[25, 26] and hydrogen abstraction – vinylacetylene addition (HAVA) pathways in combustion[27-29] and extraterrestrial environments[30] (Schemes 1 and 2). These PAHs are synthesized through systematic ring annulation reactions starting with aromatic radicals like benzyl ($C_7H_7^\bullet$), phenyl ($C_6H_5^\bullet$), and naphthyl ($C_{10}H_7^\bullet$) reacting with acetylene (C_2H_2, HACA) and vinylacetylene (C_4H_4, HAVA) with the potential of yielding ultimately *two-dimensional graphene-type nanostructures*.[31] The elementary reactions involving acetylene (HACA) involve significant entrance barriers ranging from 10 to 30 kJ mol^{-1} and hence may only operate at elevated temperatures of up to a few 1,000 K such as in combustion flames[25, 26, 32] and in circumstellar envelopes of carbon rich Asymptotic Giant Branch (AGB) stars like IRC+10216. However, most of the studied reactions of aromatic radicals with vinylacetylene (HAVA) have been found to be essentially barrierless. Overall these bimolecular reactions are characterized by the initial formation of a van-der-Waals complex, addition of the radical center to the terminal carbon atom of the vinyl (H_2C=CH-) moiety of vinylacetylene leading to resonantly stabilized free radical intermediates (RSFRs) on the doublet surface, and eventually form PAHs after isomerization via ring closure and hydrogen shift(s) terminated by atomic hydrogen loss and aromatization.[27-29, 33] Therefore, in strong contrast to HACA, PAH growth via HAVA is rapid even at ultralow temperatures such as in cold molecular clouds like the Taurus Molecular Cloud-1 (TMC-1)[33] and also in hydrocarbon rich atmospheres of planets and their moons such as Saturn's satellite Titan[27] thus contradicting prior knowledge that high temperature environments are essential in the formation and growth of aromatic structures.[34]

However, whereas a systematic understanding of the formation of two-dimensional PAHs carrying solely six-membered rings up to pyrene ($C_{16}H_{10}$) is beginning to emerge,[27] the most fundamental reaction mechanisms leading eventually to *three-dimensional nanostructures* and soot in combustion systems are still unknown.[34] This requires an intimate understanding of how the simplest building blocks – precursors to non-planar aromatic molecules - are generated in the gas phase. It is critical to point out that non-planar PAHs such as corannulene along with fullerenes

(Scheme 3) require five-membered rings as found in, for example, indene (C_9H_8) to transit planar PAHs out of the plane. The intimate knowledge of the elementary mechanisms to synthesize PAHs carrying five-membered ring(s) is therefore critical to our understanding of the early stage chemistry of how three-dimensional (bowl-shaped) nanostructures and ultimately soot particles are formed in high temperature extreme environments such as in combustion systems and also in the interstellar medium (ISM). Once again, molecular beam experiments along with electronic structure calculations have been instrumental in untangling the formation of the simplest prototype of a PAH carrying a single six- and five-membered ring: indene (C_9H_8) (Scheme 2). Here, the benzyl radical ($C_7H_7^{\bullet}$) was found to react with acetylene (C_2H_2) yielding solely indene;[35] likewise, crossed molecular beams and high temperature chemical reactor studies provided evidence that the phenyl radical reacts with allene (C_3H_4) and methylacetylene (C_3H_4) forming indene (C_9H_8)[9, 36-39] along with non-PAH isomers phenylallene (C_9H_8), 1-phenyl-1-propyne (C_9H_8), and 3-phenyl-1-propyne (C_9H_8). Supported by electronic structure calculations, the successful study of the elementary reaction of 1-naphthyl ($C_{10}H_7^{\bullet}$) with acetylene (C_2H_2) provided the very first experimental evidence of a PAH carrying two six-membered and one five-membered rings: acenaphthylene ($C_{12}H_8$).[40] Overall, these studies revealed that elementary reactions of acetylene and allene/methylacetylene with aromatic radicals can 'add' a five-membered ring to an existing six-membered ring. However, the inherent elementary steps, energy flow processes, and reaction mechanisms to form more complex PAHs carrying five-membered rings via ring annulation of existing aromatic radicals leading to benzindene isomers (Scheme 4) at the molecular level are still elusive as detailed synthetic routes have not been investigated experimentally to date. A critical PAH carrying a five-membered ring – benzindene ($C_{13}H_{10}$) - has been detected in combustion flames of toluene[41-43] and benzene[44].

Although these isomers were probed in low pressure premixed toluene/oxygen/argon,[41, 42] in atmospheric pressure ethylene,[45, 46] and in benzene flames,[44] there is a paucity in the proposed reaction mechanisms. Those considered are suggested to involve unstudied multi step reactions of benzene (C_6H_6) or phenyl ($C_6H_5^{\bullet}$) with the benzyl radical ($C_7H_7^{\bullet}$) – after hydrogen abstractions - by closure of a new five-membered ring.[42, 44] 3*H*-benz[*e*]indene is proposed to be synthesized from 1-methylnaphthalene involving hydrogen abstraction from the methyl group followed by acetylene reaction, isomerization, and hydrogen loss.[44, 47-57] Here, we elucidate both experimentally and computationally the hitherto elusive pathways to three distinct isomers of benzindene ($C_{13}H_{10}$)

(Scheme 4). This is accomplished by exploring the chemistry of the elementary reactions of the 2-naphthyl radical ($C_{10}H_7^{\bullet}$), generated via pyrolysis of its 2-iodonaphthalene precursor, with two distinct C_3H_4 isomers - allene and methylacetylene – and probing the molecular mass growth processes via ring annulation to benzindenes along with its non-indene isomers 2-(prop-2-yn-1-yl)naphthalene, 2-(prop-1-yn-1-yl)naphthalene, and 2-(propa-1,2-dien-1-yl)naphthalene. The products were detected isomer-specifically through fragment-free photoionization in a molecular beam via tunable vacuum ultraviolet (VUV) light in tandem with the detection of the ionized molecules in a reflectron time-of-flight mass spectrometer thus shedding light on the synthesis of distinct benzindene isomers under high temperature conditions relevant to combustion settings and circumstellar envelopes of carbon-rich stars. Note that naphthalene ($C_{10}H_8$) has been identified in sooting flames of non-aromatic hydrocarbon-based fuels methane (CH_4),[58] ethane (C_2H_6),[59] acetylene (C_2H_2),[60] propene (C_3H_6),[61] *n*-butane (C_4H_{10}),[62] 1,3-butadiene (C_4H_6),[63] as well as in aromatic fuels such as benzene (C_6H_6),[41, 64] toluene (C_7H_8),[41, 42, 65] styrene (C_8H_8),[41] ethylbenzene (C_8H_{10}),[41, 66] and in xylenes (C_8H_{10}).[41, 67, 68] Unimolecular decomposition of naphthalene ($C_{10}H_8$) via hydrogen loss reaction or hydrogen atom abstraction from naphthalene by another radical can lead to the 2-naphthyl radical reactant ($C_{10}H_7^{\bullet}$) in these high temperature environments.

2. Experimental

By studying the reactions of the 2-naphthyl radical ($C_{10}H_7^{\bullet}$) with methylacetylene (CH_3CCH; Organic Technologies; 99%) and allene (H_2CCCH_2; Organic Technologies; 98%) under simulated combustion conditions, we deliver experimental and computational evidence of the growth of a five-membered ring connected to a naphthalene moiety. Here, a continuous beam of 2-naphthyl radicals ($C_{10}H_7^{\bullet}$) was prepared in situ through pyrolysis of the 2-iodonaphthalene ($C_{10}H_7I$) precursor (Sigma Aldrich, 99%). In separate experiments, the precursor was seeded in pure helium (blank experiment) and in the methylacetylene as well as allene reactants at pressures of 300 Torr. Each gas mixture was then expanded into a resistively heated silicon carbide (SiC) tube ("pyrolytic reactor") held at 1275 ± 10 K (methylacetylene) and 1325 ± 10 K (allene). The hydrocarbon molecules introduced at typical pressures of 300 Torr do not only serve as a seeding gas, but also as reactants with the pyrolytically generated 2-naphthyl radicals. The products formed in the reactor were expanded supersonically, passed through a 2 mm diameter skimmer located 10 mm downstream of the pyrolytic reactor, and entered into the main chamber, which houses the Wiley–

McLaren reflectron time-of-flight mass spectrometer (ReTOF-MS). The quasi-continuous tunable vacuum ultraviolet (VUV) light from the Advanced Light Source intercepted the neutral molecular beam perpendicularly in the extraction region of the Re-TOF-MS. VUV single photon ionization is essentially a fragment-free ionization technique and is compared soft to electron impact ionization.[69] The ions formed via photoionization are extracted and detected by a multichannel plate detector. Photoionization efficiency (PIE) curves, which report ion counts as a function of photon energy with a step interval of 0.05 eV at a well-defined mass-to-charge ratio (*m/z*), were produced by integrating the signal recorded at the specific *m/z* for the species of interest from 8.00 eV to 10.00 eV. PIE calibration curves for six helium-seeded $C_{13}H_{10}$ isomers were also collected (Figure 1), to identify the products of interest observed in this work. Synthesis and characterization of 3*H*-benz[*e*]indene **p2,** 2-(prop-1-yn-1-yl)naphthalene **p4**, 2-(propa-1,2-dien-1-yl)naphthalene **p5**, and 2-(prop-2-yn-1-yl)naphthalene **p6** are described in the Electronic Supplementary Information (ESI).

3. Computational

The calculation of the energies and molecular parameters of various intermediates and transition states for the reactions of 2-naphthyl with allene and methylacetylene occurring on the $C_{13}H_{11}$ potential energy surface (PES), as well as of the reactants and possible products were carried out at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. Within this theoretical scheme, geometries were optimized and vibrational frequencies were calculated using the density functional B3LYP method with the 6-311G(d,p) method. Then, single-point total energies were improved using a series of coupled clusters CCSD(T) and second-order Møller-Plesset perturbation theory MP2 calculations, and the final energy was computed as

$$E[G3(MP2,CC)] = E[CCSD(T)/6\text{-}311G(d,p)] + E[MP2/G3Large)] - E[MP2/6\text{-}311G(d,p)] + ZPE[B3LYP/6\text{-}311G(d,p)]$$ [70-72]

The G3(MP2,CC) model chemistry approach normally provides chemical accuracy of 0.01–0.02 Å for bond lengths, 1–2º for bond angles, and 3–6 kJ mol^{-1} for relative energies of hydrocarbons, their radicals, reaction energies, and barrier heights in terms of average absolute deviations.[71] The GAUSSIAN 09[73] and MOLPRO 2010[74] program packages were employed for the ab initio calculations. Phenomenological rate constants for the 2-naphthyl + C_3H_4 reactions at different temperatures and pressures were evaluated using the Rice-Ramsperger-Kassel-Marcus Master

Equation (RRKM-ME) theoretical approach as implemented in the MESS software package.[75, 76] The Rigid-Rotor, Harmonic-Oscillator (RRHO) model was generally adopted for the calculations of densities of states and partition functions for local minima and numbers of states for transition states. For critical entrance transition states of the $C_{10}H_7$ plus C_3H_4 reactions, low-frequency normal modes corresponding to internal rotations were treated as one-dimensional hindered rotors in partition function calculations, where the corresponding vibrational frequencies were removed. Respective one-dimensional torsional potentials were calculated by scanning PESs at the B3LYP/6-311G(d,p) level of theory. Tunneling corrections using asymmetric Eckart potentials were included in rate constant calculations. We adopted collision parameters used by us earlier for RRKM-ME calculations of the prototype C_6H_5 plus C_3H_4 reactions.[77] In particular, the Lennard-Jones parameters were taken as (ε/cm^{-1}, σ/Å) = (390, 4.46) and the temperature dependence of the range parameter α for the deactivating wing of the energy transfer function was expressed as $\alpha(T) = \alpha_{300}(T/300\text{ K})^n$, with n = 0.62 and α_{300} = 424 cm^{-1}. Calculations at very low pressures emulating the zero-pressure limit took into account radiational stabilization of $C_{13}H_{11}$ intermediates. Additional details of RRKM-ME calculations can be found in our previous publications[77] and in the input file for the MESS package given in the ESI.

4. Results & Discussion

4.1. Experiments

Figure 2 displays representative mass spectra recorded at a photoionization energy of 9.50 eV for the 2-naphthyl-helium, 2-naphthyl-allene, and 2-naphthyl-methylacetylene systems. In the reference system (Fig. 2a), ion counts can be seen at mass-to-charge (*m/z*) of 128, 129, 254, and 255. Signal at *m/z* = 254 and 255 can be linked to the molecular parent and the ^{13}C counterpart of the 2-iodonaphthalene precursor ($C_{10}H_7I$, $^{13}CC_9H_7I$). The ion counts at *m/z* = 128 and 129 could be associated with molecules holding the molecular formulae $C_{10}H_8$ and $^{13}CC_9H_8$. Upon introducing allene and methylacetylene into the reactor, additional ion counts emerge in both systems at *m/z* = 142, 143, 152, 153, 166, and 167 (Figs 2b and c). Accounting for the molecular weight of the methylacetylene/allene reactants and the products, the $C_{13}H_{10}$ isomer(s) (166 amu) plus atomic hydrogen along with their ^{13}C counterpart(s) are formed via the reaction of the 2-naphthyl radical (127 amu) plus allene/methylacetylene (40 amu). Signal at *m/z* = 142, 143, 152, and 153 likely originates from C_9H_{10}, $^{13}CC_8H_{10}$, $C_{11}H_{10}$, and $^{13}CC_{10}H_{10}$, respectively.

Using PIE curves for *m/z* = 166, which is connected to the formation of $C_{13}H_{10}$ species, we now identify the structural isomer(s) synthesized in our reactor (Figure 3). These functions can be fit with a linear combination of established reference PIE curves for distinct $C_{13}H_{10}$ isomers (Figure 1). For the 2-naphthyl-allene (Fig. 3a) and 2-naphthyl-methylacetylene systems (Fig. 3c), the PIE curves at *m/z* = 166 can be both replicated with a linear combination of four reference curves of distinct $C_{13}H_{10}$ isomers. In case of the allene reactant, 3*H*-benz[*e*]indene (22 ± 5%), 1*H*-benz[*f*]indene (22 ± 5%), 2-(prop-2-yn-1-yl)naphthalene (11 ± 3%) and 2-(prop-1,2-dien-1-yl)naphthalene (45 ± 9%) are necessary to fit the experimental PIE curve with the contributions of the ion counts given in parentheses. The onset of 3*H*-benz[*e*]indene parent ion is experimentally calibrated to be 7.55 ± 0.05 eV; this corresponds well with the experimentally derived PIE curve at *m/z* = 166 with an onset of 7.60 ± 0.05 eV. On the other hand, for the methylacetylene reactant, contributions of 3*H*-benz[*e*]indene (5 ± 1%), 1*H*-benz[*f*]indene (11 ± 2%), 2-(pro-1-yn-1-yl)naphthalene (32 ± 6%) and 2-(prop-1,2-dien-1-yl)naphthalene (52 ± 10%) are necessary. For both systems, ion counts at *m/z* = 167 ($^{13}CC_{12}H_{10}$) represent the ^{13}C isotopologues of $C_{13}H_{10}$ since after scaling, the PIE graphs for *m/z* = 166 and 167 essentially overlap. It is important to highlight that in neither system, the 1*H*-benz[*e*]indene isomer was detected.

For completeness – and to provide additional information of the underlying reaction mechanism(s) – we also inspect the PIE curves at *m/z* = 142, 143, 152, and 153 (Figs. 4 and 5). The PIE curves at *m/z* = 142 can be reproduced nicely for both systems with the 2-methylnaphthalene ($C_{11}H_{10}$) molecule; this is indicative that a methyl radical recombined with the 2-naphthyl radical followed by third body stabilization (reaction (1)). The identification of 2-ethynylnaphthalene ($C_{12}H_8$) via its molecular parent ion at *m/z* = 152 and the ^{13}C counterpart ($^{13}CC_{11}H_8$) reveals two possible pathways: the recombination of 2-naphthyl with an ethynyl radical followed by a third body stabilization (reaction (2)) or reaction of 2-naphthyl with methylacetylene to the C_3H_4-branched naphthalene intermediate ($C_{13}H_{11}^{\bullet}$) followed by methyl group loss (reaction (3)). Considering the allene reactant, the formation of 2-ethynylnaphthalene via an indirect reaction mechanism through addition to allene would require at least two successive hydrogen atom shifts in the allene moiety (4.2. Computations).

(1) $$C_{10}H_7^{\bullet} + CH_3^{\bullet}\ (+M) = C_{11}H_{10}\ (+M)$$

(2) $$C_{10}H_7^{\bullet} + C_2H^{\bullet}\ (+M) = C_{12}H_8\ (+M)$$

(3) $$C_{10}H_7^{\bullet} + C_3H_4 = C_{12}H_8 + CH_3^{\bullet}$$

4.2. Computations

Our work reveals that the PAHs carrying five-member rings, 1*H*-benz[*f*]indene and 3*H*-benz[*e*]indene, along with their C_3H_3-branched naphthalene isomers, can be produced via the elementary reactions of 2-naphthyl with methylacetylene/allene. To extract the underlying reaction mechanisms and the experimental data are merged with electronic structure calculations on the potential energy surfaces (PESs) (Figure 6).

4.2.1. 2-Naphthyl - Methylacetylene

The computation reveals that the 2-naphthyl radical approaches the C1 or C2 atom of methylacetylene leading to the formation of two doublet radical intermediates **[i1]** and **[i8]** through entrance barriers of 10 and 14 kJ mol^{-1}, respectively. Passing over a barrier of 22 kJ mol^{-1}, **[i1]** isomerizes to its cis-trans isomer **[i2]**, followed by a [1,2] hydrogen shift from the methyl group to the β carbon in the side chain, leading to the formation of **[i9]** followed by cis-trans isomerization to **[i10]**. The subsequent cyclization process of **[i10]** yields **[i11]**, which depicts the carbon backbone of 1*H*-benz[*f*]indene; this reaction sequence is completed by a hydrogen atom elimination producing 1*H*-benz[*f*]indene (**p1**) through a tight exit transition state in an overall exoergic reaction (-153 kJ mol^{-1}, blue line). On the other hand, **[i2]** can isomerize via cyclization to **[i3]**, ring opening to **[i4]** and cis-trans isomerization to **[i8]**. By passing over a barrier of 12 kJ mol^{-1}, intermediate **[i8]** may isomerize to **[i5];** this intermediate undergoes a [1,4] hydrogen migration from the C1 carbon of the ring to the radical position of the side chain forming **[i6]**. A second [1,4] hydrogen shift from the methyl moiety of the side chain to the *ortho* carbon of the ring leads the isomerization of **[i6]** to **[i7]**. The CH_2 moiety in the side chain approaches the C2 of the naphthalene carbon skeleton forming intermediate **[i13]**; this species carries a three-member ring, and ring opens to **[i14]**. Alternatively, through a [1,4] hydrogen shift from the C3 of naphthyl to the C=C=C moiety, **[i14]** isomerizes to **[i15]**, which undergoes cyclization step to the 1*H*-benz[*f*]indene carbon backbones in **[i17]**. A final hydrogen atom loss from the C1 carbon atom in **[i17]** leads to the formation of 1*H*-benz[*f*]indene (**p1**) by overcoming a tight exit transition state located 18 kJ mol^{-1} above the product 1*H*-benz[*f*]indene (**p1**, green line). On the other hand, a [1,4] hydrogen shift from C1 of the naphthyl moiety to the C=C=C backbone isomerizes **[i14]** to **[i16]** followed by ring closure to **[i18]**. The subsequent hydrogen emission from C1 at the five-member ring of **[i18]** yields 3*H*-benz[*e*]indene (**p2**, green line). Let us compare both routes (blue and green lines) leading to benzindene. First, 3*H*-benz[*e*]indene (**p2**) can only be produced through the reaction sequence reactants → (**[i2]** → **[i3]** → **[i4]** →) **[i8]** → **[i5]** → **[i6]** → **[i7]** → **[i13]** → **[i14]** → **[i16]** → **[i18]** → **p2** (green line). 1*H*-benz[*f*]indene can be produced via the reaction sequence reactants → **[i2]** → **[i9]** → **[i10]** → **[i11]** → **p1** or reactants → (**[i2]** → **[i3]** → **[i4]** →) **[i8]** → **[i5]** → **[i6]** → **[i7]** → **[i13]** → **[i14]** → **[i15]** → **[i17]** → **p1** as indicated via the blue and green route, respectively. Considering the high energy transition state from **[i2]** to **[i9]** compared to **[i2]** to **[i3]**, the formation of the 1*H*-benz[*f*]indene via the sequence reactants → (**[i2]** → **[i3]** → **[i4]** →) **[i8]** → **[i5]** → **[i6]** → **[i7]** → **[i13]** → **[i14]** → **[i15]** → **[i17]** → **p1** (green pathway) should be preferred.

Except for 1*H*-benz[*f*]indene and 3*H*-benz[*e*]indene, 2-(prop-1-yn-1-yl)naphthalene (**p4**), and 2-(propa-1,2-dien-1-yl)naphthalene (**p5**) were also identified as products in 2-naphthyl – methylacetylene system. Based on the aforementioned discussion, the hydrogen loss in **[i2]** leads to the formation of 2-(prop-1-yn-1-yl)naphthalene and 2-(propa-1,2-dien-1-yl)naphthalene. Also, the [1,2] hydrogen shift in **[i2]** from the C1 to the C2 carbon of the side chain leads to **[i12]**, which may emit a hydrogen atom to generate 2-(prop-1-yn-1-yl)naphthalene (**p4**). However, the isomerization from **[i2]** to **[i12]** requires a significant barrier of 191 kJ mol^{-1} making this pathway less competitive. Moreover, 2-(prop-1-yn-1-yl)naphthalene can also be produced by the hydrogen atom loss from **[i9]**; 2-(propa-1,2-dien-1-yl)naphthalene can be generated through atomic hydrogen elimination from **[i9]** and **[i10]**. Nevertheless, due to the relatively high barrier from **[i2]** to **[i9]**, these pathways are anticipated to be less competitive. To conclude, the products **p4** and **p5** are suggested to be produced mainly from the hydrogen loss process involving intermediate **[i2]**. Besides the $C_{13}H_{10}$ products, the $C_{12}H_{10}$ product (m/z = 152), identified as 2-ethynylnaphthalene (**p7**), was a byproduct also observed experimentally. According to our PES calculation, it can be produced from the methyl-loss process from **[i8]** by overcoming a barrier of 143 kJ mol^{-1}.

4.2.2. 2-Naphthyl - Allene

In the 2-naphthyl – allene system, the approaching 2-naphthyl radical can add to the C1 and C2 carbons of allene leading to intermediates **[i14]** and **[i7]** by overcoming entrance barriers of 8 and 11 kJ mol^{-1}, respectively. 1*H*-benz[*f*]indene (**p1**) and 3*H*-benz[*e*]indene (**p2**) are produced, as discussed above, via the pathways color coded in green. The remaining products observed experimentally - 2-(propa-1,2-dien-1-yl)naphthalene (**p5**) and 2-(prop-2-yn-1-yl)naphthalene (**p6**) - are generated via a hydrogen loss from **[i14]** from C1 and C3 carbons on the side chain, respectively.

Note that upon formation of **[i14]**, only two isomerization steps to **[i17]** and **[i18]** are necessary prior to the decomposition to the benzindene molecules 1*H*-benz[*f*]indene (**p1**) and 3*H*-benz[*e*]indene (**p2**); four steps are required if **[i7]** is formed initially. On the other hand, the formation of benzindenes in the 2-naphthyl – methylacetylene system involves eight steps, among them intermediate **[i14]**, which efficiently links both surfaces. Therefore, **[i14]** likely presents a common intermediate in the formation of the benzindene molecule(s) in the reactions of the 2-naphthyl radical with both allene and methylacetylene. Considering that only two additional reaction steps are involved in the benzindene synthesis in the 2-naphthyl – allene system, but eight in the 2-naphthyl – methylacetylene reaction, benzindene(s) is/are preferentially formed in the reaction of 2-naphthyl radicals with allene as supported by the experimentally determined ion counts contributing to the PIE fits. Since the theoretically calculated yields of **p2** and 1*H*-benz[*e*]indene (**p3**) are very close to each other, a small photoionization cross section might explain the non-observation of the latter in both allene and methylacetylene systems. Note that the isomerization barrier of 2-naphthyl to 1-naphthyl is 251 kJ mol^{-1} [78] and the rate constant for the isomerization process at 1300 K and the pressure range typical for the reactor is 4.0×10^{3} s^{-1} corresponding to the lifetime of 250 ms, which is longer than the time the molecular beam spends in the reaction zone.[28] For the isomerization of allene to methylacetylene, it is even slower: 1.04×10^{2} s^{-1} at 1300 K. Thus, under our experiment conditions, the isomerization processes from allene to methylacetylene and from 2-naphthyl to 1-naphthyl do not happen.

4.2.3. Reaction rate constants and product branching ratios

Figure 7 shows RRKM-ME total rate constants for the reactions of 2-naphthyl with methylacetylene and allene calculated at the high-pressure (HP) and zero-pressure limits and at finite pressures (panels (a) and (d), respectively) as well as rate constants for individual bimolecular product channels at 0.03 atm characteristic inside the micro reactor (panels (b) and (e)) and in the limit of zero pressure (panels (c) and (f)) – here the calculations were actually performed at p = 10^{-10} and 10^{-15} atm, which gave nearly identical results just showing a convergence to a zero pressure. Both reactions are predicted to be relatively fast at elevated temperatures with the HP rate constants increasing from 2.1×10^{-13} to 4.1×10^{-11} cm^3 molecule cm^3 $molecule^{-1}$ for the methylacetylene reaction and from 1.8×10^{-13} to 3.8×10^{-11} cm^3 molecule cm^3 $molecule^{-1}$ for the allene reaction in the 500-2500 K temperature range, with the former reaction being slightly slower than the latter. The rate constant dependence on pressure appears to be rather weak, as the fall-off behaviors begins to be observed around 800 K and at the highest considered temperature of 2500 K, the zero-pressure (and all finite-pressure) rate constants are factors of 1.6 and 2.3 lower than those at the HP limit for methylacetylene and allene, respectively. Earlier,[77] we reported RRKM-ME rate constants for the phenyl plus methylacetylene/propyne reactions, which are the prototype reactions for the growth of an extra five-member ring on a six-member ring. These rate constants are also shown for comparison in Figs. 7(a) and (d). For methylacetylene, the reaction with 2-naphthyl appears to be from a factor of 4.0 (500 K) to a factor of 2.1 (2500 K) faster than that with phenyl, whereas for allene the difference is somewhat larger, from a factor of 6.9 to 2.1 in the 500-2500 K temperature range. The difference is slightly beyond the expected accuracy for one-dimensional master equation treatment (a factor of 2) and can apparently be attributed to the fact that the entrance barriers for the 2-naphthyl + methylacetylene (10 and 14 kJ mol^{-1}) and 2-naphthyl + allene (8 and 11 kJ mol^{-1}) reactions are computed here to be a little lower than the corresponding barriers for phenyl + methylacetylene (14 and 26 kJ mol^{-1}) and phenyl + allene (11 and 15 kJ mol^{-1}). Since the differences in the barrier heights are within the expected accuracy of our G3(MP2,CC) approach, we can conclude that the rate constants for phenyl + C_3H_4 and 2-naphthyl + C_3H_4 are similar within the error bars of the present calculations. Hence, the rate constants for the prototype phenyl reactions can be used in kinetic modeling to describe a general reaction of PAH growth by a five-member ring via C_3H_4 addition to a radical site on a six-member ring, keeping in mind the rate constants may increase by factors 2-3 with the growth of the attacked aryl radical at the temperatures relevant to combustion.

The calculated rate constants for individual product channels and product branching ratios presented in Table S1 in ESI show a strong temperature and pressure dependence. At p = 0.03 atm characteristic for the micro reactor conditions, the three-ring products **p1**, **p2**, and **p3** are predicted to be preferably formed among bimolecular products in the reaction of 2-naphthyl with allene up to the temperature of 1200 K. In the meantime, at low temperatures, up to 1100 K, collisional stabilization of the $C_{13}H_{11}$ intermediates **[i14]** and **[i7]** is favored over the formation of the bimolecular products. Above 1200 K, the formation of the two-ring-side-chain products, especially **p6** (27-82%), followed by **p7** (10-11% to 5%) and **p5** (5-8%) takes over and represents most preferable reaction channels. Nevertheless, at 1300 K, which is the highest temperature in the micro reactor in the present work, the predicted relative yields of **p1**, **p2**, and **p3** – 16.5%, 9.4%, and 9.3%, respectively, are still significant. Alternatively, the reaction of 2-naphthyl with methylacetylene is calculated to have a lower tendency to form the three-ring products. Here, the collisional stabilization of $C_{13}H_{11}$, mostly **[i1]**, dominates the reaction below 800 K and at higher temperatures the main product is **p4** (26-61%) followed by **p7** (12-31%) and **p5** (3-7%). The overall calculated yield of the three-ring products **p1-p3** is 0.77% at 1300 K and it further decreases with temperature. The RRKM-ME calculation results are in qualitative agreement with experiment except of the non-observation of **p3**, which is predicted to have a similar branching ratio to that of **p2**. In the meantime, a direct quantitative comparison between theory and experiment is not warranted for several reasons. First, the absolute photoionization cross sections of the product isomers are unknown. Second, the temperature and pressure distribution inside the micro reactor is not uniform and hence, the reaction takes place under different conditions as the molecules traverse the reactor. Third, there is sufficient time for secondary reactions to occur; in particular, the more thermodynamically favorable three-ring products can be produced via secondary H-assisted isomerization of **p4-p6** products similar to how indene can be formed via H-assisted isomerization of the primary *c*-C_6H_5-C_3H_3 ring-side-chain products of the C_6H_5 + C_3H_4 reaction.[77]

Theoretical calculations allow us to predict how the reaction outcome would change under different pressures. For instance, while considering $p = 1$ atm typical for combustion, we find that the collisional stabilization of the $C_{13}H_{11}$ complexes prevails up to higher temperatures, 1300 and 1000 K for the allene and methylacetylene reactions, respectively. At higher temperatures, the formation of the two-ring-side-chain products is preferable (**p6** followed by **p5** and **p7** for allene and **p4** followed by **p7** and **p5** for methylacetylene). At the typical combustion temperature of 1500 K, the calculated total yield of **p1-p3** is about 19% for allene and only ~0.2% for methylacetylene, with **p1** being somewhat more preferable product than **p2** and **p3**. The decrease of pressure, on the contrary, should increase the yield of the three-ring aromatic products, mostly because they are favored enthalpically and are disfavored entropically and the collisional stabilization of $C_{13}H_{11}$ becomes less and less probable as the pressure drops. In the limit of zero-pressure, where only radiational stabilization of $C_{13}H_{11}$ is possible, the formation of **p1-p3** prevails in the 2-naphthyl + allene reaction in the temperature range of 300-1200 K and in the 2-naphthyl + methylacetylene reaction in the range of 300-500 K (Table S1). Although the reactions exhibits entrance barriers and are not realistic in molecular clouds at temperatures about 10 K, they would be feasible at the temperatures characteristic for circumstellar envelopes of carbon rich AGB stars, with the rate constants being in the range of 1.9×10^{-14} – 5.0×10^{-12} (allene) and 1.6×10^{-14} – 7.4×10^{-12} (methylacetylene) cm^3 $molecule^{-1}$ s^{-1} at T = 300-1500 K. Since the formation of the three-ring aromatic products is favored at very low pressures, the reactions of 2-naphthyl with the C_3H_4 isomers may play a more important role in the PAH growth in circumstellar envelopes than in combustion on Earth.

It should be noted that in combustion systems, molecular mass growth processes are counterbalanced by degradation of PAH radicals by molecular oxygen as demonstrated in the phenyl – molecular oxygen system.[79-81] Here, anthracenyl and/or phenanthrenyl radical reactions with molecular oxygen could also lead via ring contraction of a six-membered ring to a five-membered ring forming benzindenes. In the combustion of coal, the amount of indene benzologues increased with the oxygen concentration. Wornat et al. stated that benz[*f*]indene could be formed via molecular oxygen addition to the 1- or 2-anthryl radical, followed by carbon monoxide elimination and hydrogen loss (Scheme 6).[82] This oxy radical pathway could dominate above 900 K as analogous to the reaction of phenyl plus molecular oxygen.[83, 84] Similarly, phenanthrenyl radicals can also lead to $C_{13}H_{10}$ isomers (Scheme 7). Moreover, Norinaga et al.[85, 86] proposed the mechanism for benz[*f*]indene formation from pyrolysis of unsaturated light hydrocarbons, however, recent experiments in our laboratory could not support this conclusion.[87]

5. Conclusion

Our combined experimental and computational studies revealed critical mass growth processes involving the addition of a five-membered ring to an aromatic aryl radical (2-naphthyl) leading to two distinct three-membered ring PAHs carrying two six- and one five-membered ring: 3*H*-benz[*e*]indene and 1*H*-benz[*f*]indene. The underlying reaction mechanisms involve the initial addition of the 2-naphthyl radical with its radical center to the π-electron density of the allene and methylacetylene reactants through entrance barriers between 8-11 and 10-14 kJ mol^{-1}, followed by extensive isomerization (hydrogen shifts, ring closure), and termination via atomic hydrogen losses accompanied by aromatization in overall exoergic reaction with both surfaces connected via intermediate **[i14]**. The reaction mechanisms essentially mirror the formation of the indene molecule (C_9H_8) in the phenyl-allene and phenyl-methylacetylene systems[9, 88, 89] and suggest that the second aromatic ring in the 2-naphthyl radical acts as a spectator. These findings propose that if in a polycyclic aromatic hydrocarbon, hydrogen abstraction from a six-membered ring leads to a PAH radical, this radical can react with allene or methylacetylene through ring annulation. Based on electronic structure calculations, Mebel et al.[77] et al. predicted that once PAHs carrying a five-membered ring lose a hydrogen atom from the latter, the cyclopentadienyl radical moiety may react with a methyl radical (CH_3) through ring expansion leading eventually to a six-membered ring (Scheme 5). Therefore, the mass growth via the methylacetylene/allene reaction with aryl radicals leading first via ring annulation to a 5-membered ring followed by methyl radical induced ring expansion may represent a strong alternative to ring annulation of aryl radicals via HACA through reaction with two acetylene molecules in high temperature environments.

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Author Contributions

R.I.K. designed the experiment; L.Z., M.P., B.X., U.A. and W.L. carried out the experimental measurements; M.A. supervised the experiment; L.Z. performed the data analysis; A.D.O., V.N.A. and A.M.M. carried out the theoretical analysis; A.H.H. and S.F.W. synthesized the compounds, A.M.M., and M.A. discussed the data; R.I.K., A.M.M. and L.Z. wrote the manuscript.

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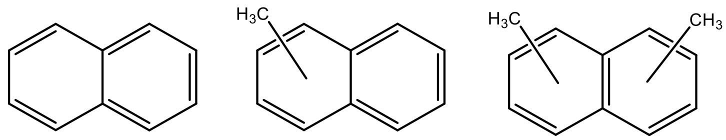
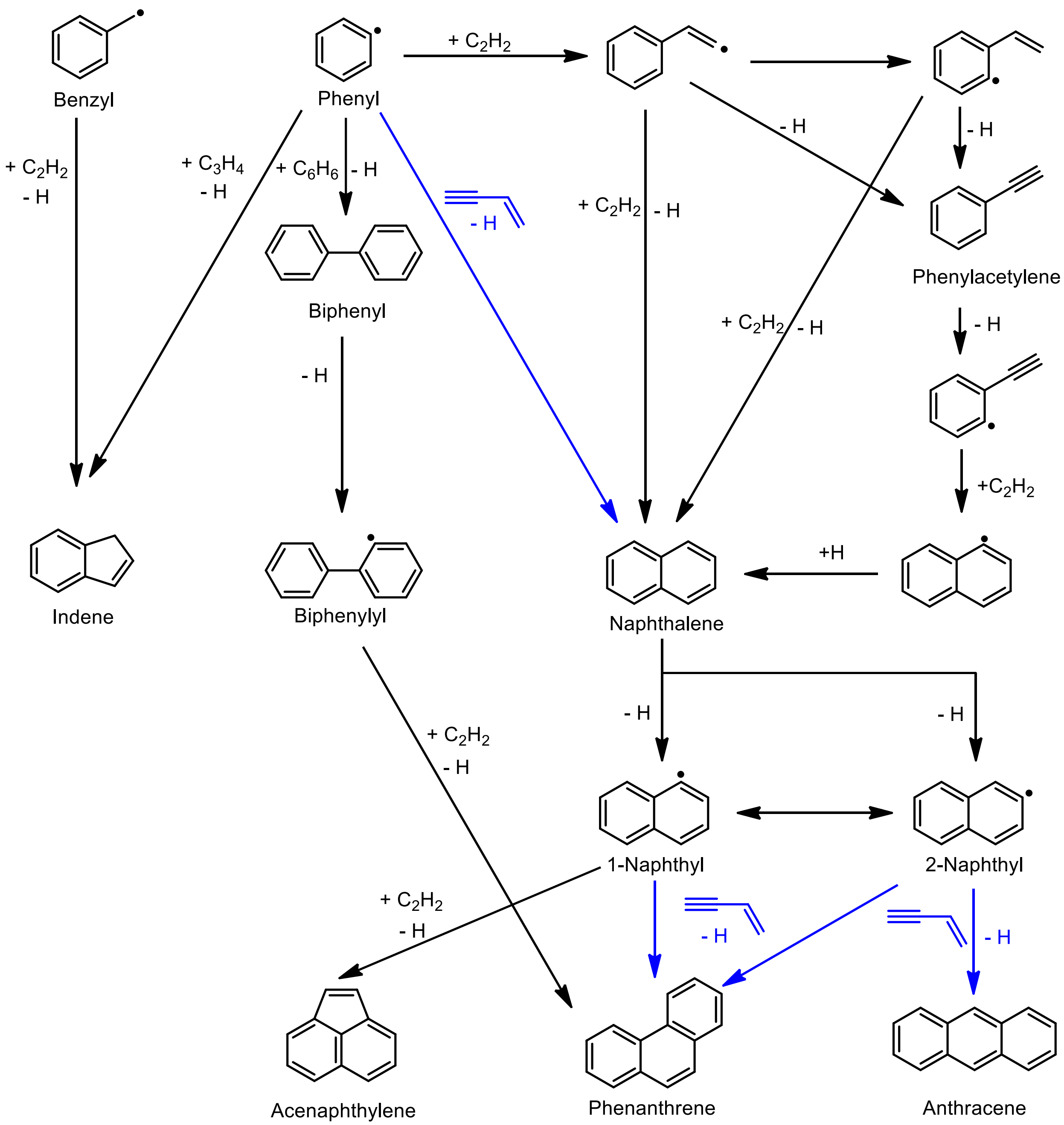
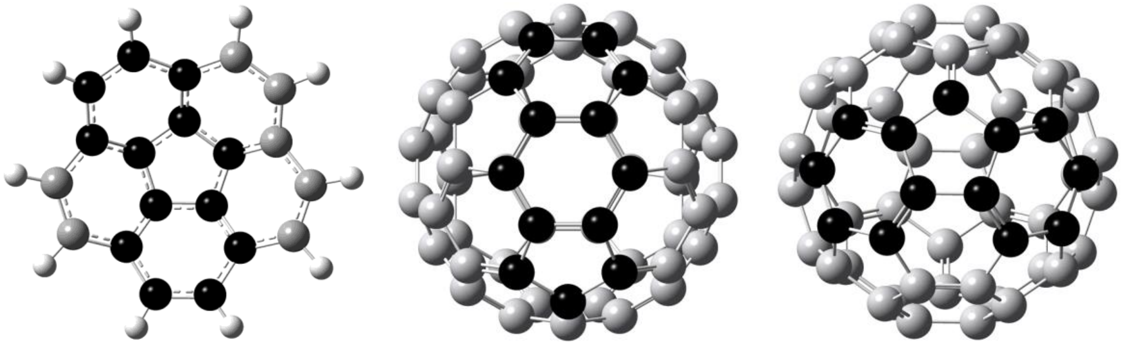


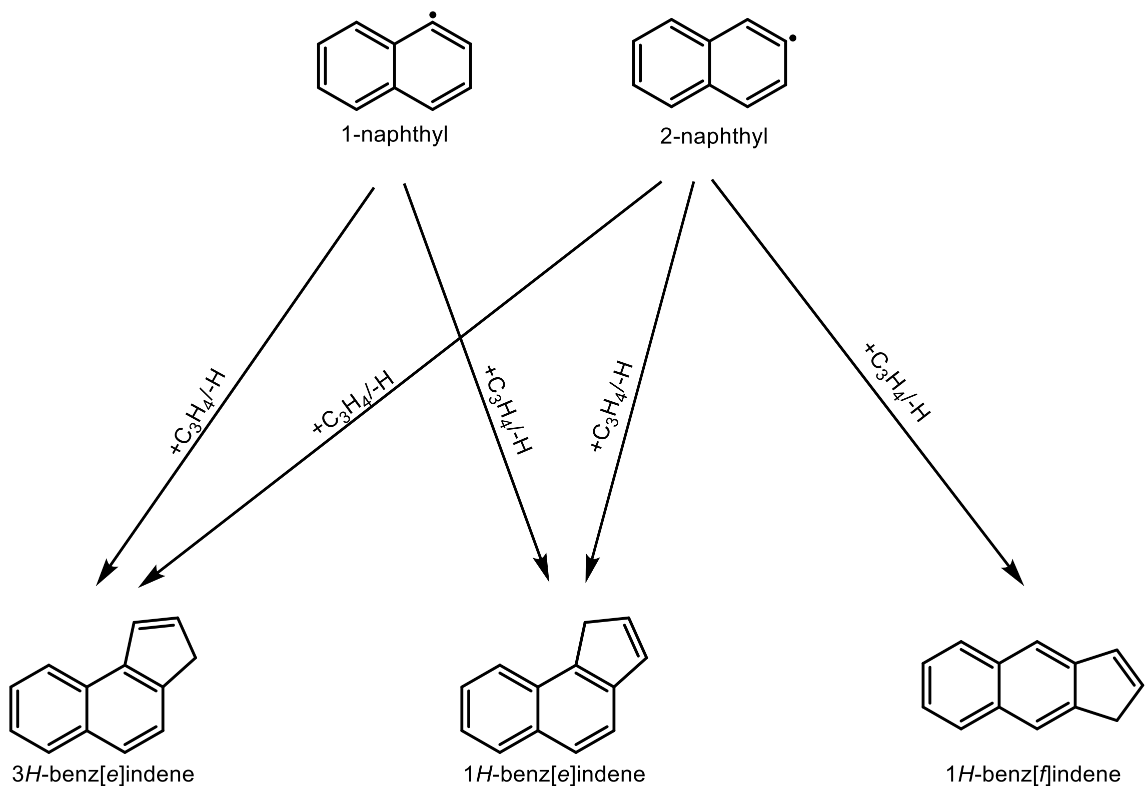
Scheme 1: Prototype polycyclic aromatic hydrocarbon naphthalene together with (di)methyl substituted counterparts formed in the reactions of phenyl-type radicals (phenyl, tolyl).



Scheme 2: Experimentally verified possible mass growth processes to bi- and tricyclic PAHs via the hydrogen abstraction – acetylene addition (HACA) (black) and the barrier-less hydrogen abstraction – vinylacetylene addition (HAVA) pathways (blue). Note that biphenyl is formed via hydrogen abstraction – phenyl addition.



Scheme 3: The role of fluorene and benzindene backbones (black) as building blocks of corannulene (left) and fullerenes (center, right).



Scheme 4: Proposed stepwise formation of prototype tricyclic PAHs carrying a single five-membered ring. In combustion flames, naphthyl radicals are generated via unimolecular decomposition of or via hydrogen abstraction from naphthalene.

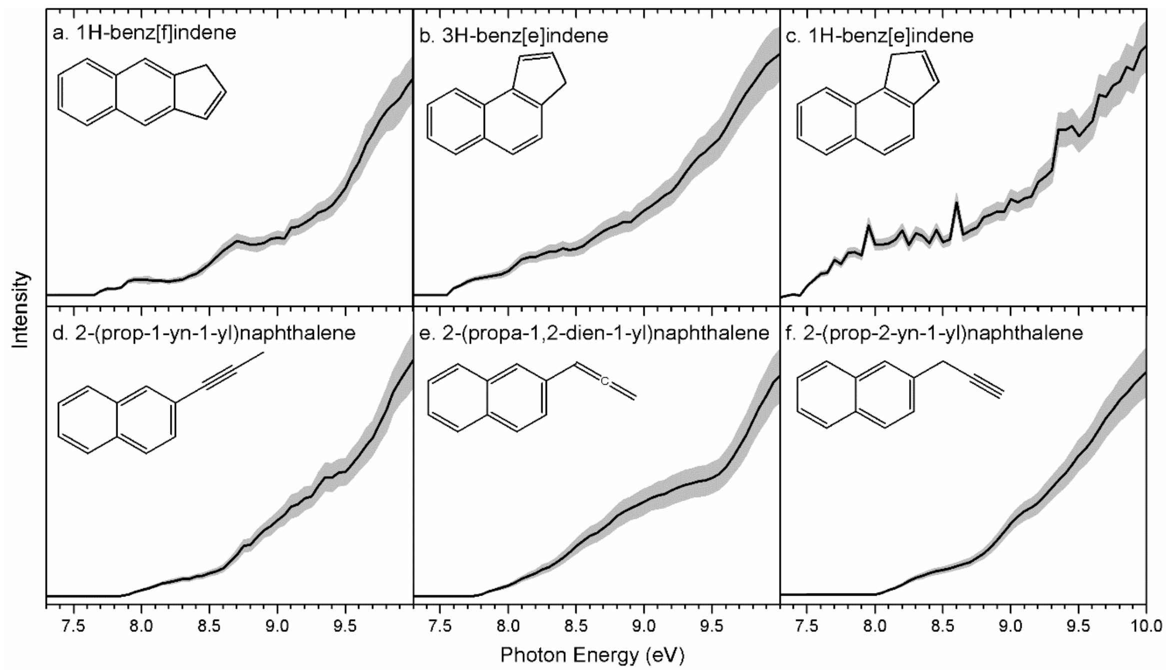


Figure 1. PIE calibration curves for distinct $C_{13}H_{10}$ isomers: 1*H*-benz[*f*]indene (**p1**; 7.75 ± 0.05 eV), 3*H*-benz[*e*]indene (**p2**; 7.55 ± 0.05 eV), 1*H*-benz[*e*]indene (**p3**; 7.45 ± 0.05 eV), 2-(prop-1-yn-1-yl)naphthalene (**p4**; 7.85 ± 0.05 eV), 2-(propa-1,2-dien-1-yl)naphthalene (**p5**; 7.75 ± 0.05 eV) and 2-(prop-2-yn-1-yl)naphthalene (**p6**; 8.00 ± 0.05 eV). The values in the parenthesis indicates the ionization energies. The overall error bars (grey area) consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

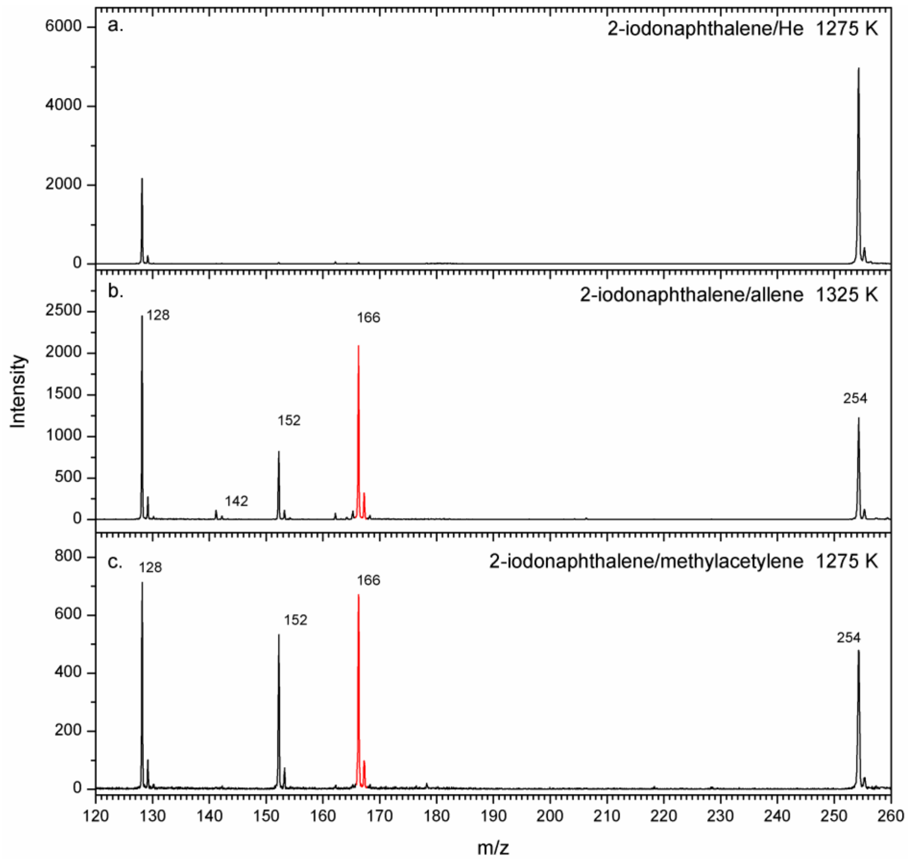


Figure 2. Comparison of photoionization mass spectra recorded at a photon energy of 9.50 eV and various reactor temperatures. (a) 2-iodonaphthalene ($C_{10}H_7I$) - helium (He) system at 1275 K; (b) 2-iodonaphthalene ($C_{10}H_7I$) - allene (C_3H_4) system at 1325 K; and (c) 2-iodonaphthalene ($C_{10}H_7I$) - methylacetylene (C_3H_4) system at 1275 K. The mass peaks of the newly formed $C_{13}H_{10}$ (*m/z* = 166) species along with the ^{13}C-counterparts (*m/z* = 167) are highlighted in red.

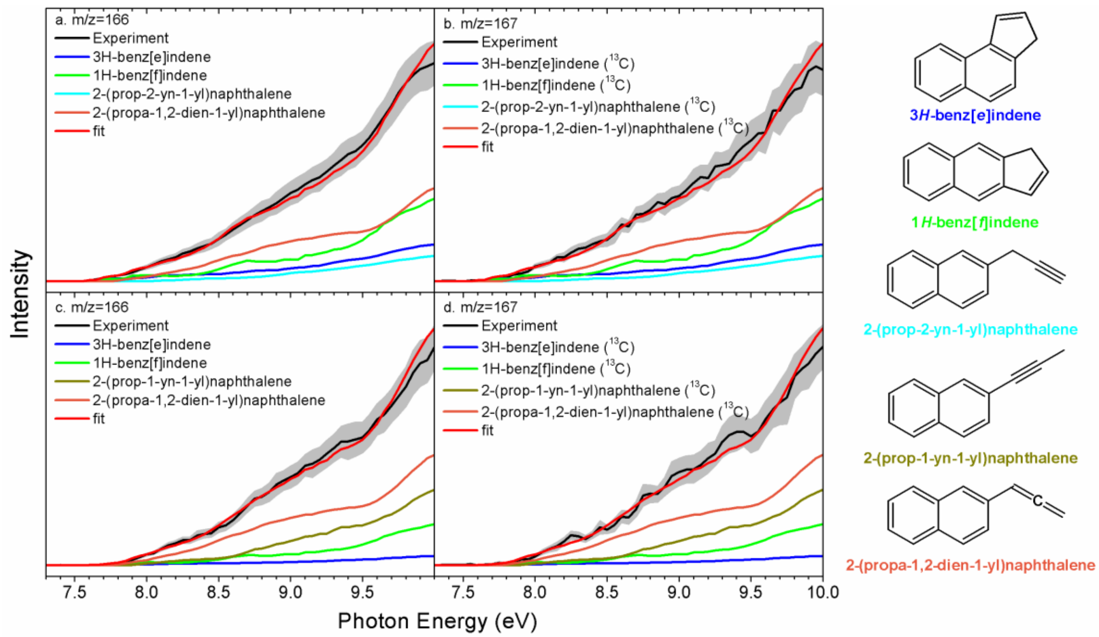


Figure 3. Photoionization efficiency (PIE) curves for reaction systems of (a) and (b): 2-naphthyl ($C_{10}H_7^{\bullet}$) + allene (C_3H_4); (c) and (d): 2-naphthyl ($C_{10}H_7^{\bullet}$) + methylacetylene (C_3H_4). Black: experimentally derived PIE curves; colored lines (green, blue, purple and dark yellow): reference PIE curves; red lines: overall fit. The overall error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

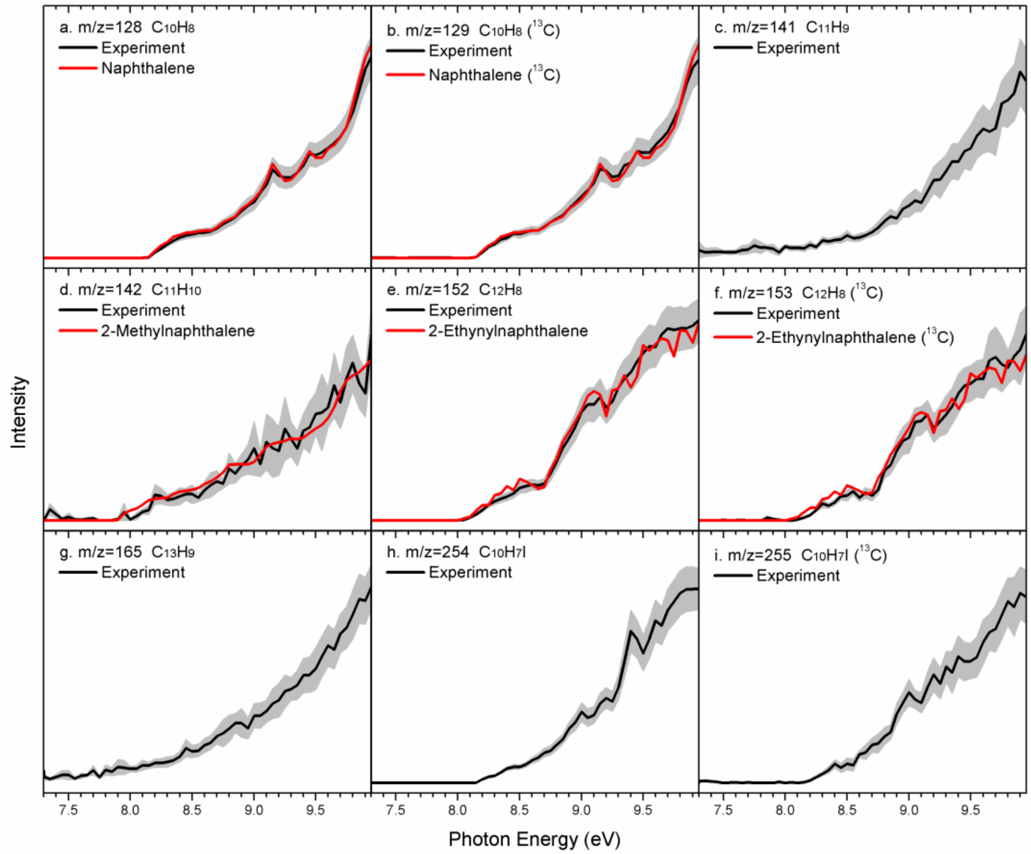


Figure 4. Photoionization efficiency (PIE) curves in the reaction of 2-naphthyl ($C_{10}H_7^{\bullet}$) and allene (C_3H_4) along with the experimental errors (gray area) and the reference PIE curves (red lines). In the high temperature condition, methyl (CH_3) is produced in the pyrolysis process, reacting with 2-naphthyl radical to produce 2-methylnaphthalene (m/z = 142). Moreover, 2-methylnaphthalene will loss a hydrogen atom to yield a radical with the resonantly-stabilized structure (m/z = 141). Acetylene is also one of major small products formed in the pyrolysis. It can add to 2-naphthyl radical followed by H-loss to form 2-ethynylnaphthalene (m/z = 152). Besides, 2-ethynylnaphthalene can also be produced from the CH_3-loss from intermediate **[i8]** by overcoming a barrier of 143 kJ mol^{-1}. Product at m/z = 165 may be the H-loss product from 1*H*-benz[*f*]indene and 3*H*-benz[*e*]indene. It is also a resonantly-stabilized species. Species at m/z = 254 and 255 are the precursor and the ^{13}C counterparts.

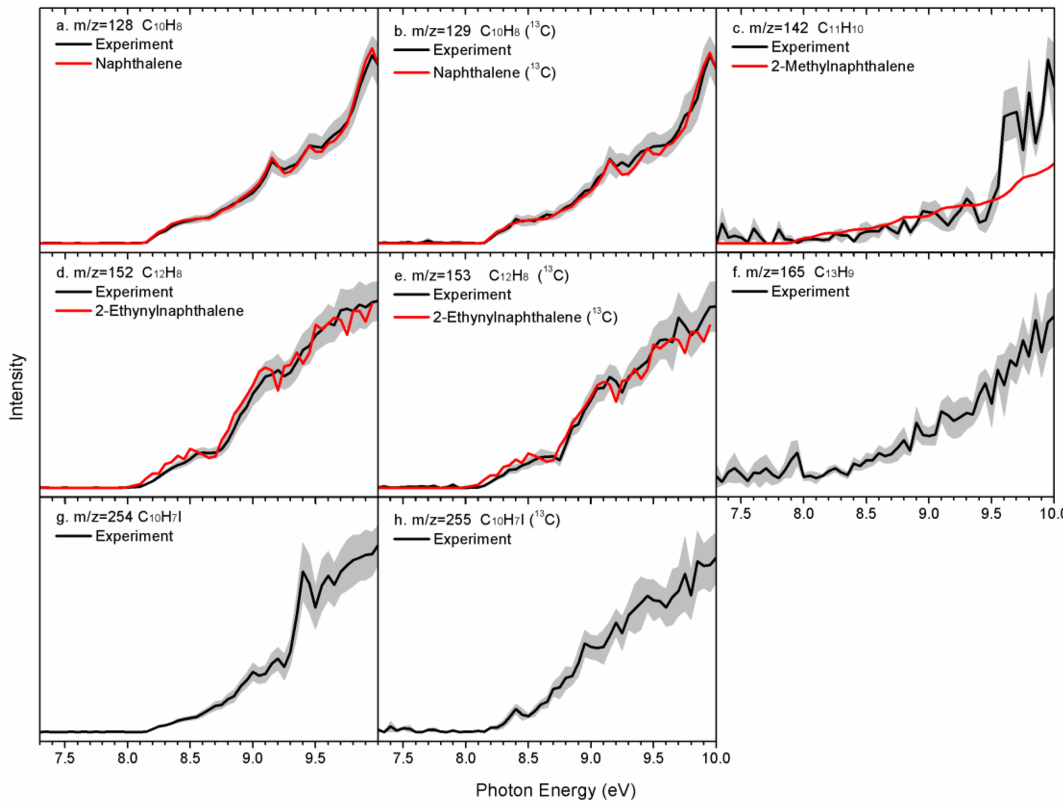


Figure 5. Photoionization efficiency (PIE) curves in the reaction of 2-naphthyl ($C_{10}H_7^{\bullet}$) and methylacetylene (C_3H_4) along with the experimental errors (gray area) and the reference PIE curves (red lines). In the high temperature condition, methyl (CH_3) is produced in the pyrolysis process, reacting with 2-naphthyl radical to produce 2-methylnaphthalene (*m/z* = 142). Due to the low production at *m/z* =142, the PIE curve is relatively worse compared with that in 2-naphthyl – allene system. Acetylene is one of major small products formed in the pyrolysis. It can add to 2-naphthyl radical followed by H-loss to form 2-ethynylnaphthalene (*m/z* = 152). Besides, 2-ethynylnaphthalene can also be produced from the CH_3-loss from intermediate **[i8]** by overcoming a barrier of 143 kJ mol^{-1}. Product at *m/z* = 165 may be the H-loss products from 1*H*-benz[*f*]indene and 3*H*-benz[*e*]indene. It is also a resonantly-stabilized species. Species at *m/z* = 254 and 255 are the precursor and the ^{13}C counterpart.

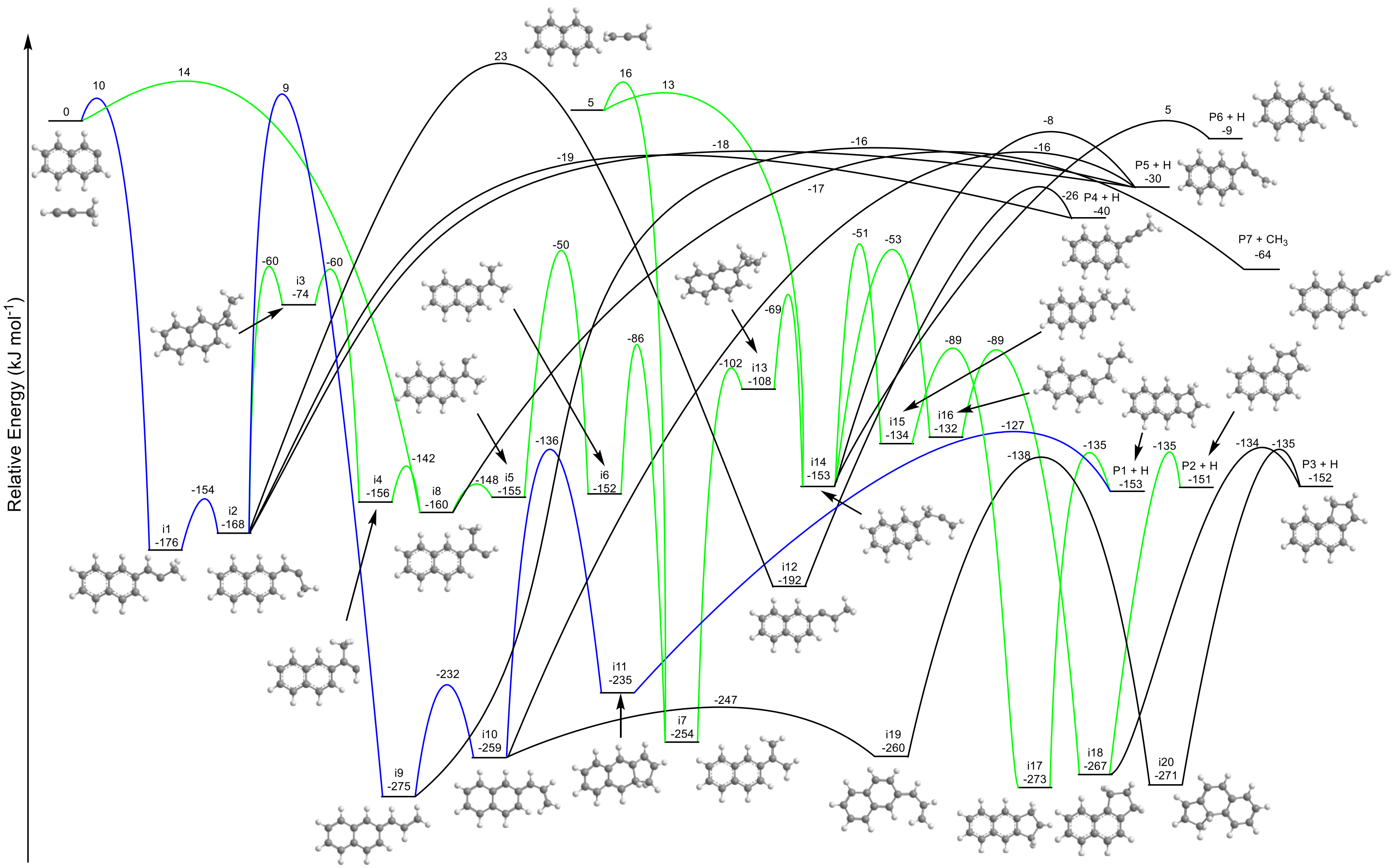


Figure 6. Potential energy surface (PES) for the 2-naphthyl ($C_{10}H_7^{\bullet}$) reaction with allene/methylacetylene (C_3H_4). This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory for the channels leading to 1*H*-benz[*f*]indene (**p1**), 3*H*-benz[*e*]indene (**p2**), 1*H*-benz[*e*]indene (**p3**), 2-(prop-1-yn-1-yl)naphthalene (**p4**), 2-(propa-1,2-dien-1-yl)naphthalene (**p5**), 2-(prop-2-yn-1-yl)naphthalene (**p6**) and 2-ethynyl-naphthalene (**p7**). The relative energies are given in kJ mol^{-1}. Blue and green lines indicate two alternative pathways leading to the formation of benzindene molecules (**p1** and **p2**) observed in the present work.

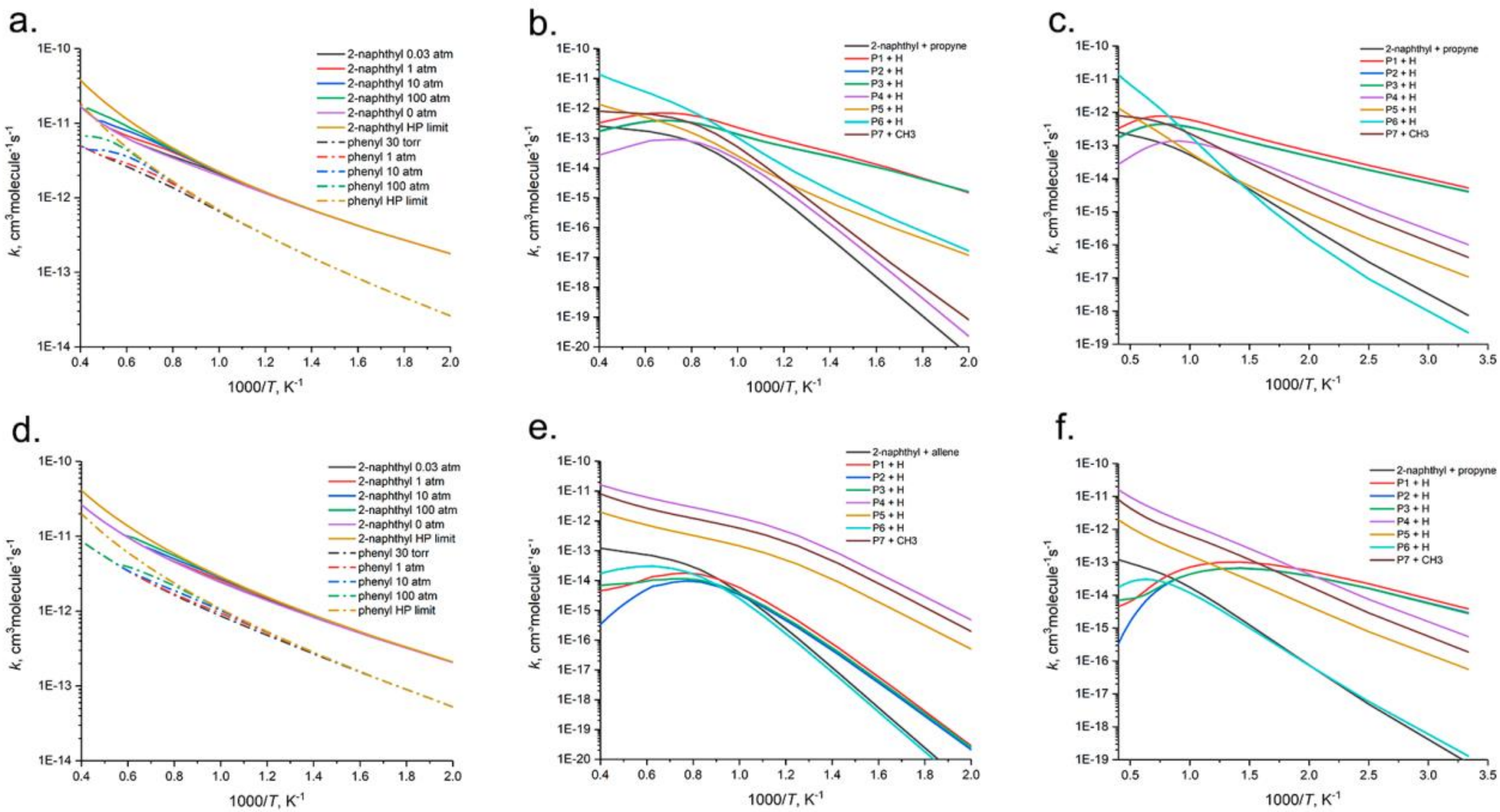
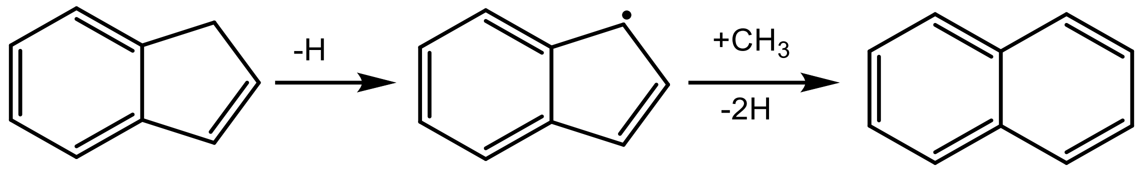
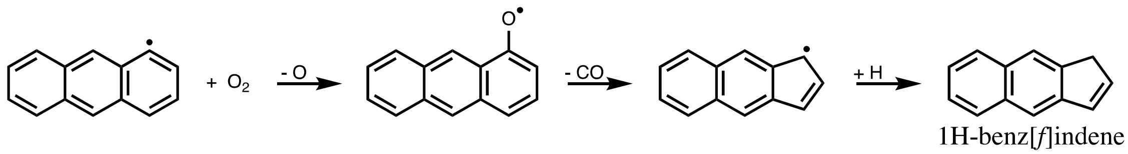


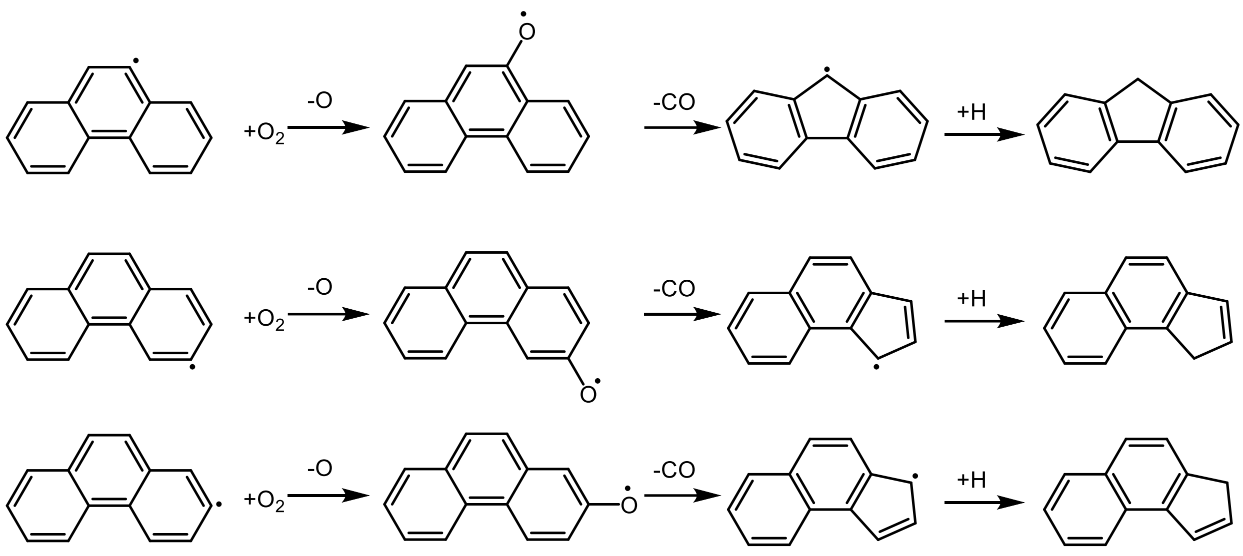
Figure 7. Calculated total and individual rate constants for the 2-naphthyl + C_3H_4 reactions: a. total rate constants for 2-naphthyl + allene at different pressures, total rate constants for the phenyl + allene reaction (Ref. 77) are shown for comparison; b. and c. rate constants for various bimolecular product channels of the 2-naphthyl + allene reaction at 0.03 atm and at zero pressure limit, respectively; d. total rate constants for 2-naphthyl + methylacetylene at different pressures, total rate constants for the phenyl + methylacetylene reaction (Ref. 77) are shown for comparison; e. and f. rate constants for various bimolecular product channels of the 2-naphthyl + methylacetylene reaction at 0.03 atm and at zero pressure limit, respectively. Note that the blue (**p2**) and green (**p3**) curves merge at panels b. and c.



Scheme 5. Conversion of indene to naphthalene via H-loss and the reaction with methyl radical (CH_3).



Scheme 6. Formation of 1*H*-benz[*f*]indene from 1-anthryl radical via the reaction with O_2, CO loss and hydrogen addition processes.



Scheme 7. Formation of PAHs carrying a five-member ring from phenanthrenyl radicals via the reaction with O_2, CO loss and hydrogen addition processes.

How to Add a Five-Membered Ring to Polycyclic Aromatic Hydrocarbons (PAHs) – Molecular Mass Growth of the 2-Naphthyl Radical ($C_{10}H_7$) to Benzindenes ($C_{13}H_{10}$) as a Case Study

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ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1. Calculated product branching ratios of the 2-naphthyl + C_3H_4 reactions at various pressures and temperatures.

(a) 2-naphthyl + allene, 0.03 atm.

T, K	methyl-acetylene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i7**	**i14**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	0.01%	0.01%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	17.85%	81.34%	0.23%	0.46%	0.03%	0.00%	99.88%
400	0.00%	0.12%	0.16%	0.16%	0.00%	0.00%	0.00%	0.00%	0.00%	36.48%	60.49%	0.86%	1.72%	0.43%	0.00%	99.56%
500	0.00%	0.83%	0.90%	0.88%	0.00%	0.01%	0.01%	0.00%	0.00%	61.78%	30.98%	2.40%	2.22%	2.61%	0.02%	97.37%
600	0.00%	2.62%	2.26%	2.23%	0.00%	0.03%	0.06%	0.00%	0.00%	78.79%	9.95%	2.17%	1.89%	7.11%	0.09%	92.80%
700	0.00%	4.75%	3.45%	3.39%	0.01%	0.09%	0.22%	0.02%	0.02%	83.75%	2.29%	1.19%	0.80%	11.59%	0.34%	88.05%
800	0.04%	6.50%	4.23%	4.16%	0.10%	0.22%	0.69%	0.18%	0.04%	82.67%	0.48%	0.43%	0.22%	14.90%	1.20%	83.85%
900	0.18%	8.28%	5.09%	5.00%	0.37%	0.54%	1.97%	0.82%	0.06%	77.49%		0.12%	0.05%	18.37%	3.70%	77.72%
1000	0.55%	10.74%	6.41%	6.29%	0.91%	1.20%	4.89%	2.38%	0.09%	66.50%		0.03%	0.01%	23.43%	9.38%	66.64%
1100	1.15%	13.68%	8.01%	7.85%	1.58%	2.25%	10.22%	4.92%	0.11%	50.22%		0.01%	0.00%	29.54%	18.96%	50.35%
1200	1.84%	15.94%	9.20%	9.02%	2.11%	3.58%	17.92%	7.74%		32.62%				34.16%	31.36%	32.62%
1300	2.38%	16.53%	9.44%	9.25%	2.23%	4.93%	26.97%	9.88%		18.38%				35.22%	44.01%	18.38%
1400	2.68%	15.53%	8.77%	8.59%	2.03%	6.08%	36.14%	10.92%		9.23%				32.89%	55.18%	9.23%
1500	2.78%	13.60%	7.61%	7.45%	1.69%	6.95%	44.60%	11.05%		4.26%				28.67%	64.28%	4.26%
1600	2.81%	11.81%	6.57%	6.42%	1.44%	7.65%	52.40%	10.91%						24.80%	72.39%	
1700	2.65%	9.51%	5.24%	5.12%	1.07%	8.00%	58.40%	10.01%						19.87%	77.48%	
1800	2.49%	7.64%	4.18%	4.08%	0.80%	8.22%	63.46%	9.12%						15.90%	81.61%	
1900	2.33%	6.15%	3.34%	3.27%	0.61%	8.34%	67.68%	8.29%						12.75%	84.92%	
2000	2.17%	4.97%	2.69%	2.62%	0.47%	8.38%	71.17%	7.53%						10.28%	87.55%	
2100	2.02%	4.04%	2.18%	2.13%	0.37%	8.38%	74.05%	6.84%						8.35%	89.63%	
2200	1.88%	3.32%	1.78%	1.74%	0.29%	8.33%	76.44%	6.22%						6.83%	91.29%	
2300	1.75%	2.74%	1.47%	1.43%	0.24%	8.26%	78.44%	5.67%						5.64%	92.61%	
2400	1.63%	2.29%	1.22%	1.19%	0.19%	8.18%	80.12%	5.18%						4.70%	93.67%	
2500	1.51%	1.93%	1.03%	1.00%	0.16%	8.09%	81.53%	4.75%						3.95%	94.53%	

(b) 2-naphthyl + allene, 1 atm.

T, K	methyl-acetylene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i7**	**i14**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	11.64%	88.33%	0.00%	0.00%	0.00%	0.00%	99.97%
400	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	17.07%	82.80%	0.03%	0.05%	0.00%	0.00%	99.94%
500	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	23.52%	75.84%	0.18%	0.00%	0.01%	0.00%	99.55%
600	0.00%	0.05%	0.06%	0.06%	0.00%	0.01%	0.02%	0.00%	0.00%	33.98%	63.70%	0.85%	1.14%	0.18%	0.02%	99.67%
700	0.00%	0.35%	0.39%	0.39%	0.00%	0.04%	0.11%	0.00%	0.00%	49.54%	44.63%	2.02%	2.27%	1.13%	0.16%	98.46%
800	0.00%	1.31%	1.25%	1.23%	0.00%	0.14%	0.45%	0.00%	0.00%	64.68%	24.94%	3.05%	2.92%	3.79%	0.60%	95.59%
900	0.00%	3.01%	2.43%	2.39%	0.01%	0.33%	1.26%	0.03%	0.01%	73.75%	11.70%	2.83%	2.24%	7.83%	1.62%	90.53%
1000	0.03%	4.86%	3.41%	3.35%	0.03%	0.63%	2.78%	0.13%	0.02%	76.61%	5.00%	1.90%	1.23%	11.63%	3.57%	84.76%
1100	0.10%	6.41%	4.09%	4.01%	0.10%	1.10%	5.36%	0.44%	0.03%	76.60%		1.10%	0.63%	14.51%	6.98%	78.36%
1200	0.27%	7.41%	4.45%	4.36%	0.21%	1.76%	9.46%	1.15%	0.08%	70.10%		0.50%	0.24%	16.22%	12.58%	70.93%
1300	0.58%	8.17%	4.73%	4.64%	0.41%	2.67%	15.53%	2.38%		60.52%		0.23%	0.10%	17.54%	20.99%	60.85%
1400	1.00%	8.78%	4.95%	4.84%	0.58%	3.79%	23.64%	3.97%		48.40%				18.57%	31.97%	48.40%
1500	1.43%	8.84%	4.93%	4.83%	0.69%	4.99%	33.12%	5.56%		35.56%				18.60%	44.35%	35.56%
1600	1.78%	8.45%	4.67%	4.57%	0.72%	6.10%	42.84%	6.79%		23.99%				17.69%	56.44%	23.99%
1700	2.02%	7.67%	4.22%	4.12%	0.68%	6.98%	51.74%	7.49%		15.02%				16.01%	66.89%	15.02%
1800	2.12%	6.70%	3.66%	3.57%	0.61%	7.60%	59.21%	7.69%		8.79%				13.93%	75.11%	8.79%
1900	2.33%	6.20%	3.37%	3.29%	0.62%	8.33%	67.55%	8.30%						12.86%	84.82%	0.00%
2000	2.17%	4.99%	2.70%	2.64%	0.48%	8.38%	71.10%	7.54%						10.33%	87.50%	0.00%
2100	2.02%	4.05%	2.18%	2.13%	0.37%	8.37%	74.02%	6.84%						8.37%	89.61%	0.00%
2200	1.88%	3.32%	1.78%	1.74%	0.30%	8.33%	76.43%	6.22%						6.84%	91.28%	0.00%
2300	1.75%	2.75%	1.47%	1.43%	0.24%	8.26%	78.43%	5.67%						5.65%	92.61%	0.00%
2400	1.63%	2.29%	1.22%	1.19%	0.19%	8.18%	80.11%	5.18%						4.70%	93.67%	0.00%
2500	1.51%	1.93%	1.03%	1.00%	0.16%	8.09%	81.53%	4.75%						3.96%	94.53%	0.00%

(c) 2-naphthyl + allene, zero-pressure limit.

T, K	methyl-acetylene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i7**	**i14**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	27.84%	21.71%	21.37%	0.54%	0.06%	0.00%	0.22%		28.25%				70.92%	0.82%	28.25%
400	0.04%	36.17%	26.24%	25.97%	1.93%	0.22%	0.01%	0.92%		8.48%				88.39%	3.08%	8.48%
500	0.20%	38.21%	26.67%	26.35%	4.15%	0.50%	0.08%	2.31%		1.52%				91.23%	7.05%	1.52%
600	0.56%	37.54%	25.24%	24.90%	6.34%	0.86%	0.35%	4.21%						87.68%	11.76%	0.00%
700	1.09%	36.09%	23.46%	23.11%	7.64%	1.25%	1.08%	6.28%						82.66%	16.26%	0.00%
800	1.67%	34.50%	21.77%	21.42%	7.92%	1.73%	2.68%	8.31%						77.69%	20.64%	0.00%
900	2.20%	32.61%	20.06%	19.72%	7.41%	2.33%	5.53%	10.15%						72.38%	25.42%	0.00%
1000	2.62%	30.25%	18.21%	17.89%	6.46%	3.08%	9.87%	11.61%						66.35%	31.03%	0.00%
1100	2.91%	27.42%	16.20%	15.90%	5.36%	3.94%	15.70%	12.59%						59.51%	37.58%	0.00%
1200	3.06%	24.21%	14.07%	13.80%	4.27%	4.85%	22.71%	13.03%						52.08%	44.86%	0.00%
1300	3.10%	20.82%	11.94%	11.70%	3.31%	5.74%	30.42%	12.96%						44.46%	52.43%	0.00%
1400	3.06%	17.50%	9.91%	9.71%	2.51%	6.53%	38.27%	12.50%						37.12%	59.82%	0.00%
1500	2.95%	14.43%	8.09%	7.92%	1.89%	7.18%	45.77%	11.78%						30.44%	66.61%	0.00%
1600	2.81%	11.74%	6.52%	6.38%	1.41%	7.67%	52.55%	10.92%						24.64%	72.55%	0.00%
1700	2.66%	9.48%	5.22%	5.10%	1.06%	8.01%	58.47%	10.01%						19.80%	77.55%	0.00%
1800	2.49%	7.62%	4.17%	4.08%	0.80%	8.23%	63.49%	9.12%						15.87%	81.64%	0.00%
1900	2.33%	6.14%	3.34%	3.26%	0.61%	8.34%	67.69%	8.29%						12.74%	84.93%	0.00%
2000	2.17%	4.97%	2.69%	2.62%	0.47%	8.38%	71.17%	7.53%						10.28%	87.56%	0.00%
2100	2.02%	4.04%	2.18%	2.12%	0.37%	8.38%	74.05%	6.84%						8.34%	89.64%	0.00%
2200	1.88%	3.32%	1.78%	1.74%	0.29%	8.33%	76.44%	6.22%						6.83%	91.29%	0.00%
2300	1.75%	2.74%	1.47%	1.43%	0.24%	8.26%	78.44%	5.67%						5.64%	92.61%	0.00%
2400	1.63%	2.29%	1.22%	1.19%	0.19%	8.18%	80.12%	5.18%						4.70%	93.67%	0.00%
2500	1.51%	1.93%	1.03%	1.00%	0.16%	8.09%	81.53%	4.75%						3.95%	94.53%	0.00%

(d) 2-naphthyl + methylacetylene, 0.03 atm.

T, K	allene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i5**	**i7**	**i8**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	96.67%		0.00%	3.33%	0.00%	0.00%	0.00%	0.00%	100.00%
400	0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	94.04%		0.05%	5.89%	0.00%	0.00%	0.00%	0.02%	99.98%
500	0.00%	0.00%	0.00%	0.00%	0.23%	0.02%	0.00%	0.09%	90.93%		0.37%	8.36%	0.31%	0.68%	0.00%	0.35%	100.00%
600	0.00%	0.00%	0.00%	0.00%	2.17%	0.23%	0.00%	0.97%	84.98%		1.52%	9.83%			0.00%	3.38%	96.33%
700	0.00%	0.01%	0.00%	0.00%	10.17%	1.10%	0.00%	4.63%	69.86%		5.19%	9.02%			0.02%	15.90%	84.07%
800	0.01%	0.04%	0.02%	0.03%	25.78%	2.81%	0.01%	11.66%	44.62%	6.28%	8.73%				0.08%	40.25%	59.62%
900	0.05%	0.11%	0.07%	0.08%	42.11%	4.64%	0.03%	18.79%	21.32%	3.35%	9.41%				0.26%	65.57%	34.08%
1000	0.16%	0.24%	0.14%	0.15%	52.96%	5.90%	0.10%	23.32%	9.48%		7.51%				0.53%	82.29%	16.99%
1100	0.35%	0.35%	0.20%	0.22%	58.62%	6.61%	0.21%	25.45%	3.24%		4.74%				0.77%	90.89%	7.98%
1200	0.55%	0.39%	0.22%	0.25%	61.87%	7.06%	0.33%	26.59%			2.73%				0.86%	95.85%	2.73%
1300	0.70%	0.35%	0.19%	0.23%	62.81%	7.24%	0.39%	26.84%			1.25%				0.77%	97.28%	1.25%
1400	0.77%	0.27%	0.14%	0.18%	63.31%	7.35%	0.41%	27.03%			0.53%				0.60%	98.10%	0.53%
1500	0.78%	0.20%	0.10%	0.14%	63.52%	7.42%	0.38%	27.24%			0.22%				0.44%	98.57%	0.22%
1600	0.78%	0.16%	0.07%	0.12%	63.56%	7.47%	0.35%	27.49%							0.35%	98.87%	0.00%
1700	0.73%	0.10%	0.04%	0.09%	63.48%	7.50%	0.29%	27.76%							0.24%	99.03%	0.00%
1800	0.69%	0.07%	0.03%	0.07%	63.32%	7.52%	0.24%	28.06%							0.17%	99.14%	0.00%
1900	0.65%	0.05%	0.02%	0.06%	63.12%	7.53%	0.20%	28.38%							0.13%	99.22%	0.00%
2000	0.61%	0.04%	0.01%	0.05%	62.88%	7.53%	0.17%	28.72%							0.10%	99.29%	0.00%
2100	0.57%	0.03%	0.01%	0.04%	62.61%	7.53%	0.14%	29.07%							0.08%	99.34%	0.00%
2200	0.54%	0.03%	0.00%	0.04%	62.32%	7.53%	0.11%	29.43%							0.07%	99.39%	0.00%
2300	0.51%	0.02%	0.00%	0.03%	62.01%	7.52%	0.09%	29.80%							0.06%	99.43%	0.00%
2400	0.48%	0.02%	0.00%	0.03%	61.69%	7.50%	0.08%	30.20%							0.05%	99.46%	0.00%
2500	0.46%	0.02%	0.00%	0.03%	61.34%	7.48%	0.06%	30.61%							0.04%	99.50%	0.00%

(e) 2-naphthyl + methylacetylene, 1 atm.

T, K	allene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i5**	**i7**	**i8**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	96.70%		0.00%	3.30%			0.00%	0.00%	100.00%
400	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	94.19%		0.00%	5.81%			0.00%	0.00%	100.00%
500	0.00%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	91.72%		0.01%	8.25%			0.00%	0.01%	99.99%
600	0.00%	0.00%	0.00%	0.00%	0.09%	0.01%	0.00%	0.04%	89.36%		0.06%	10.43%			0.00%	0.14%	99.85%
700	0.00%	0.00%	0.00%	0.00%	0.71%	0.08%	0.00%	0.35%	86.51%		0.28%	12.05%			0.00%	1.14%	98.85%
800	0.00%	0.00%	0.00%	0.00%	3.61%	0.40%	0.00%	1.76%	80.81%	12.48%	0.90%				0.00%	5.77%	94.20%
900	0.00%	0.00%	0.00%	0.00%	11.63%	1.29%	0.00%	5.45%	68.43%	11.16%	1.99%				0.00%	18.37%	81.58%
1000	0.01%	0.01%	0.00%	0.01%	24.98%	2.80%	0.00%	11.24%	49.47%	8.41%	3.00%				0.01%	39.02%	60.88%
1100	0.03%	0.02%	0.01%	0.01%	39.26%	4.43%	0.02%	17.16%	30.21%	5.35%	3.39%				0.04%	60.87%	38.95%
1200	0.09%	0.04%	0.02%	0.03%	50.27%	5.72%	0.05%	21.81%	18.61%		3.25%				0.08%	77.85%	21.86%
1300	0.20%	0.06%	0.03%	0.05%	62.52%	7.15%	0.10%	26.60%			3.18%				0.14%	96.37%	3.18%
1400	0.33%	0.08%	0.03%	0.06%	63.14%	7.29%	0.16%	26.84%			2.00%				0.17%	97.43%	2.00%
1500	0.45%	0.08%	0.03%	0.07%	63.46%	7.38%	0.20%	27.11%			1.20%				0.18%	98.15%	1.20%
1600	0.54%	0.07%	0.03%	0.07%	63.52%	7.44%	0.22%	27.40%			0.69%				0.17%	98.58%	0.69%
1700	0.59%	0.06%	0.02%	0.06%	63.46%	7.48%	0.22%	27.71%			0.38%				0.15%	98.87%	0.38%
1800	0.61%	0.06%	0.02%	0.06%	63.31%	7.51%	0.20%	28.03%			0.20%				0.14%	99.05%	0.20%
1900	0.65%	0.05%	0.02%	0.06%	63.12%	7.53%	0.20%	28.38%							0.13%	99.22%	0.00%
2000	0.61%	0.04%	0.01%	0.05%	62.88%	7.53%	0.17%	28.72%							0.10%	99.29%	0.00%
2100	0.57%	0.03%	0.01%	0.04%	62.61%	7.53%	0.14%	29.07%							0.08%	99.34%	0.00%
2200	0.54%	0.03%	0.00%	0.04%	62.32%	7.53%	0.11%	29.43%							0.07%	99.39%	0.00%
2300	0.51%	0.02%	0.00%	0.03%	62.01%	7.52%	0.09%	29.80%							0.06%	99.43%	0.00%
2400	0.48%	0.02%	0.00%	0.03%	61.69%	7.50%	0.08%	30.20%							0.05%	99.46%	0.00%
2500	0.46%	0.02%	0.00%	0.03%	61.34%	7.48%	0.06%	30.61%							0.04%	99.50%	0.00%

(f) 2-naphthyl + methylacetylene, zero-pressure limit.

T, K	allene	**p1**	**p2**	**p3**	**p4**	**p5**	**p6**	**p7**	**i1**	**i5**	**i7**	**i8**	**i17**	**i18**	3-ring total	2-ring total	stabilization
300	0.00%	23.64%	18.07%	17.17%	3.40%	0.34%	0.00%	1.15%			35.86%	0.02%			58.88%	4.90%	35.88%
400	0.01%	30.21%	22.05%	21.83%	10.15%	1.05%	0.01%	3.94%			10.72%				74.10%	15.15%	10.72%
500	0.04%	27.16%	19.17%	18.95%	21.34%	2.25%	0.04%	9.08%			1.99%				65.28%	32.69%	1.99%
600	0.11%	20.06%	13.71%	13.54%	33.69%	3.60%	0.10%	15.18%							47.31%	52.57%	0.00%
700	0.24%	13.15%	8.73%	8.62%	43.91%	4.77%	0.19%	20.38%							30.50%	69.26%	0.00%
800	0.41%	8.17%	5.27%	5.21%	51.13%	5.64%	0.31%	23.85%							18.66%	80.93%	0.00%
900	0.58%	4.94%	3.11%	3.08%	55.87%	6.24%	0.41%	25.76%							11.13%	88.29%	0.00%
1000	0.72%	2.96%	1.81%	1.81%	58.94%	6.66%	0.49%	26.61%							6.58%	92.70%	0.00%
1100	0.82%	1.76%	1.05%	1.07%	60.91%	6.94%	0.53%	26.90%							3.89%	95.29%	0.00%
1200	0.87%	1.05%	0.61%	0.64%	62.17%	7.14%	0.54%	26.98%							2.31%	96.82%	0.00%
1300	0.88%	0.63%	0.36%	0.39%	62.93%	7.28%	0.51%	27.02%							1.38%	97.74%	0.00%
1400	0.86%	0.39%	0.21%	0.25%	63.36%	7.37%	0.46%	27.11%							0.84%	98.30%	0.00%
1500	0.82%	0.24%	0.12%	0.17%	63.54%	7.43%	0.40%	27.27%							0.53%	98.65%	0.00%
1600	0.78%	0.16%	0.07%	0.12%	63.56%	7.47%	0.35%	27.49%							0.35%	98.87%	0.00%
1700	0.73%	0.10%	0.04%	0.09%	63.48%	7.50%	0.29%	27.76%							0.24%	99.03%	0.00%
1800	0.69%	0.07%	0.03%	0.07%	63.32%	7.52%	0.24%	28.06%							0.17%	99.14%	0.00%
1900	0.65%	0.05%	0.02%	0.06%	63.12%	7.53%	0.20%	28.38%							0.13%	99.22%	0.00%
2000	0.61%	0.04%	0.01%	0.05%	62.88%	7.53%	0.17%	28.72%							0.10%	99.29%	0.00%
2100	0.57%	0.03%	0.01%	0.04%	62.61%	7.53%	0.14%	29.07%							0.08%	99.34%	0.00%
2200	0.54%	0.03%	0.00%	0.04%	62.32%	7.53%	0.11%	29.43%							0.07%	99.39%	0.00%
2300	0.51%	0.02%	0.00%	0.03%	62.01%	7.52%	0.09%	29.80%							0.06%	99.43%	0.00%
2400	0.48%	0.02%	0.00%	0.03%	61.69%	7.50%	0.08%	30.20%							0.05%	99.46%	0.00%
2500	0.46%	0.02%	0.00%	0.03%	61.34%	7.48%	0.06%	30.61%							0.04%	99.50%	0.00%

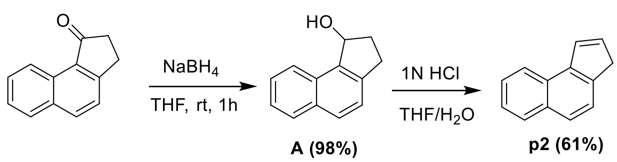
Synthesis of $C_{13}H_{10}$ isomers

General information

^{1}H (400 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded at ambient temperature in solution of $CDCl_3$. Reaction progress was monitored by TLC on Merck Kieselgel 60-F254 sheets with product detection by 254 nm light. Products were purified by column chromatography using Merck Kiselgel 60 (230-400 mesh). Reagent grade chemicals were used and solvents were dried by reflux and distillation from CaH_2 under N_2 unless otherwise specified.

Synthesis of 3*H*-benz[e]indene p2

The 3*H*-benz[a]indene[1,2] **p2** was synthesized by $NaBH_4$ reduction of commercially available 2,3-dihydro-1*H*-cyclopenta[a]naphthalene-1-one **(Scheme 1)** and β-elimination of the resulted secondary alcohol **A** with aqueous HCl.



Scheme 1. Synthesis of 3*H*-cyclopenta[a]naphthalene **p2**.

2,3-dihydro-1*H*-cyclopenta[a]naphthalene; A.

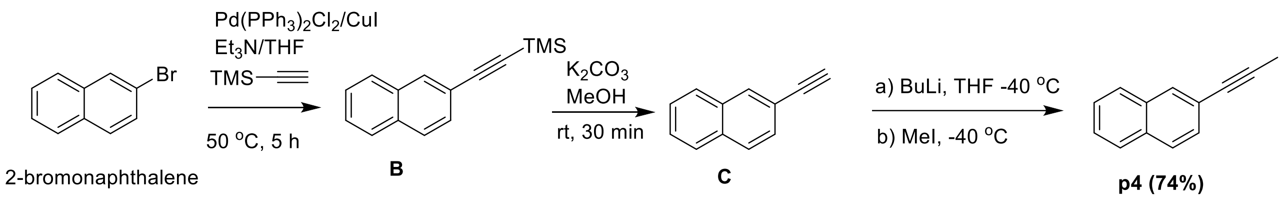
$NaBH_4$ (98 mg, 2.58 mmol) was added portion wise to a stirred solution of commercially available 2,3-dihydro-1*H*-cyclopenta[a]naphthalene-1-one (470 mg, 2.58 mmol) in dry MeOH/THF (2;1) at 0 ^{o}C (ice-bath). After 5 min, the reaction mixture was allowed to warm to ambient temperature and stirring was continued for 1 h. Water (1 mL) was then added to quench the reaction. The mixture was concentrated under reduced pressure and extracted with EtOAc. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was column chromatographed (EtOAc in hexane 10-20%) to give 2,3-dihydro-1*H*-cyclopenta[a]naphthalene **A** (465 mg, 98%) as a white solid: ^{1}H NMR δ 1.80 (s, 1H), 2.15-2.23 (m, 1H), 2.56-2.65 (m, 1H), 2.95-3.02 (m, 1H), 3.26-3.34 (m, 1H), 5.79 (d, J = 4.8 Hz, 1H), 7.40 (d, , J = 8.4 Hz, 1H), 7.44-7.48 (m, 1H), 7.52-7.56 (m, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 31.06, 35.48, 75.97, 123.52, 124.02, 125.29, 126.73, 128.66, 129.61, 130.32, 133.19, 139.29, 141.78.

3*H*-benz[e]indene; p2.

The secondary alcohol **A** (440 mg, 2.39 mmol) was dissolved in THF/H_2O (20 mL, 1:1). Aqueous 1N HCl (6.0 mL, 6 mmol) was then added and the reaction mixture was refluxed at 105 ^{o}C for 6 h. After removing THF, the reaction mixture was transferred to a separatory funnel and extracted with EtOAc. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give 3*H*-benz[a]indene **p2** (240 mg, 61%) as a white solid: ^{1}H NMR δ 3.59 (s, 2H), 6.77 (d, *J* = 5.6 Hz, 1H), 7.46-7.56 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ 40.51, 122.57, 123.95, 124.89, 125.02, 125.70, 127.99, 128.50, 129.70, 132.74, 134.40, 141.12, 141.38.

Synthesis of 2-(prop-1-yn-1-yl)naphthalene p4

The 2-(prop-1-yn-1-yl)naphthalene **p4** was synthesized by Sonogashira coupling between 2-bromonaphthalene and TMS-acetylene (**Scheme 2**) followed by desilylation. The resulted 2-ethynylnaphthalene **C** was converted to alkynide with BuLi and methylated with MeI yielding 2-(prop-1-yn-1-yl)naphthalene **p4**.[3]



Scheme 2. Synthesis of 2-(prop-1-yn-1-yl)naphthalene **p4**.

Trimethyl(naphthalen-2-ylethynyl)silane; B.

$Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol) and Cu(I)I (19.1 mg, 0.1mmol) were added to anhydrous THF (10 mL) and anhydrous Et_3N (1.5 mL, 1090 mg, 10.7 mmol) placed in flame-dried round bottom flask equipped with a stir bar. Then 2-bromonaphthalene (1035 mg, 5.0 mmol) was added followed by TMS-acetylene (832 µL, 575 mg, 5.85 mmol). The resulting mixture was stirred at 50 °C for 5 h [progress of the reaction was monitored by TLC (hexane)]. The reaction mixture was then diluted with hexane and filtered through a short pad of silica. Volatiles were evaporated and the residue was column chromatographed (n-hexane) to give trimethyl(naphthalen-2-ylethynyl)silane **B** (500 mg, 45%) as a light yellow solid: ^{1}H NMR δ 0.29 (s, 9H), 7.46-7.52 (m, 3H), 7.75-7.78 (m, 3H), 8.00 (s, 1H); ^{13}C NMR δ 0.17, 94.69, 105.62, 120.61, 126.65, 126.87, 127.89, 127.94, 128.00, 128.74, 132.15, 133.05, 133.07.

2-Ethynylnaphthalene; C.

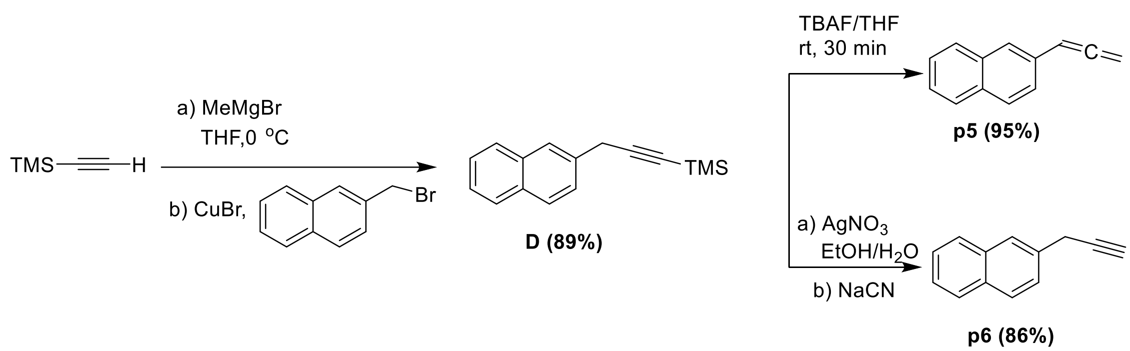
Anhydrous K_2CO_3 (300 mg, 2.2 mmol) was added to a stirred solution of **B** (480 mg, 2.14 mmol) in 10 mL MeOH at room temperature. After for 30 min, volatiles were evaporated and the residue was column chromatographed (*n*-hexane) to give **C** (300 mg, 92%) as a light yellow solid: ^{1}H NMR δ 3.15 (s, 1H), 7.49-7.55 (m, 3H), 7.78-7.84 (m, 3H), 8.04 (s, 1H); ^{13}C NMR δ 77.53, 84.17, 119.56, 126.76, 127.05, 127.92, 127.93, 128.17, 128.70, 132.46, 133.00, 133.21.

2-(Prop-1-yn-1-yl)naphthalene; p4.

A stirring solution of terminal alkyne **C** (204 mg, 1.34 mmol) in dry THF (10 mL) was cooled to -40 ^{o}C and *n*-BuLi (1.6 M/hexane, 1.70 mL, 2.72 mmol) was added. After 1 h, iodomethane (176 μL, 400 mg, 2.82 mmol) was added dropwise at -40 ^{o}C and stirred for 1 h at room temperature. The mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give 2-(Prop-1-yn-1-yl)naphthalene **p4** (160 mg, 74%) as a gummy solid: ^{1}H NMR δ 2.12 (s, 2H), 7.45-7.51 (m, 3H), 7.76-7.82 (m, 3H), 7.93 (s, 1H); ^{13}C NMR δ 4.54, 80.25, 86.34, 121.54, 126.38, 126.48, 127.72, 127.82, 127.96, 128.80, 131.14, 132.63, 133.22.

Synthesis of 2-(propa-1,2-dien-1-yl)naphthalene p5 and 2-(prop-2-yn-1-yl)naphthalene p6

The 2-(propa-1,2-dien-1-yl)naphthalene **p5** and 2-(prop-2-yn-1-yl)naphthalene **p6** were synthesized from the commercially available 2-bromomethylnaphthalene by modifying reported protocols.[4,5] Thus, treatment of trimethylsilylacetylene with MeMgBr generate alkynide which was reacted with 2-bromomethylnaphthalene (**Scheme 1**) in presence of CuBr to give **D**. Then treatment of **D** with TBAF in THF at rt gave expected product **p5.** On the other hand, treatment of **D** with $AgNO_3$/NaCN in EtOH/H_2O at rt gave expected isomeric product **p6.**



Sheme 3. Synthesis of 2-(propa-1,2-dien-1-yl)naphthalene **p5** and 2-(prop-2-yn-1-yl)naphthalene **p6**.

Trimethyl(3-(naphthalene-yl)prop-1-yn-yl)silane; D.

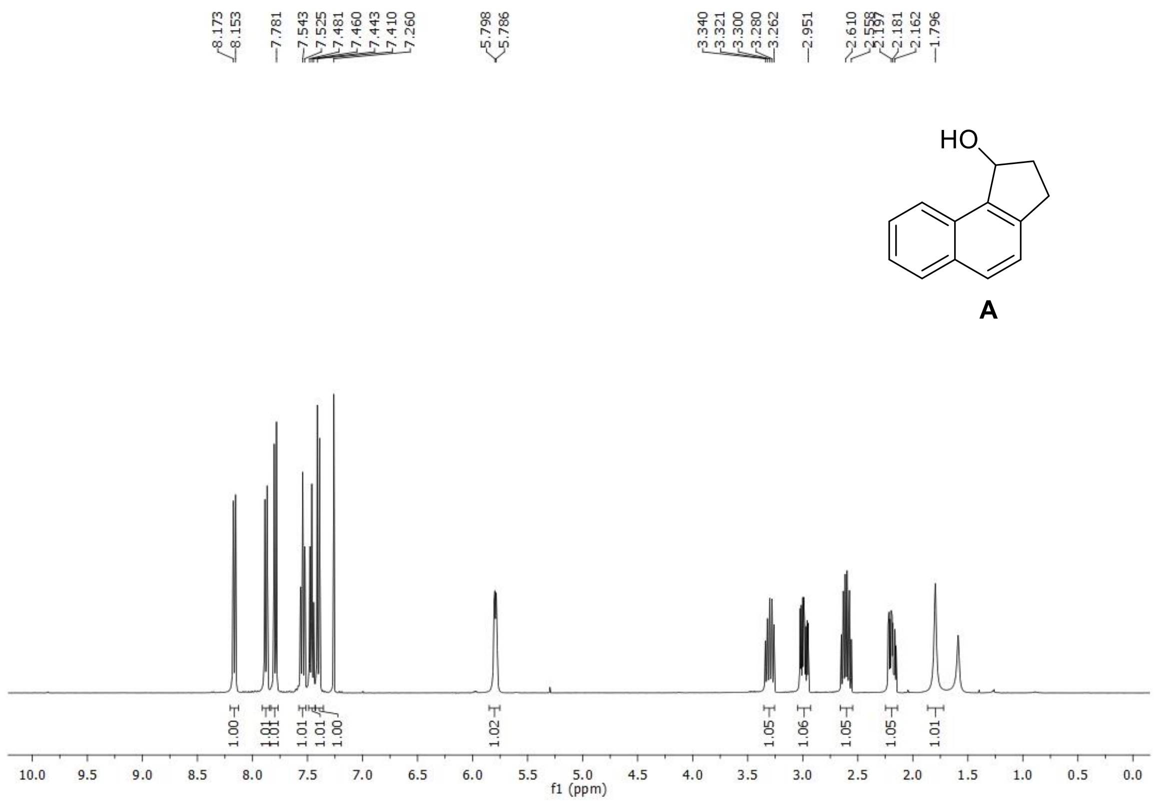
To a stirred solution of trimethylsilylacetylene (1.4 mL, 966.0 mg, 10.0 mmol) in dry THF (5 mL) was added dropwise MeMgBr (3 M/Et_2O, 3.4 mL, 10.0 mmol) at 0 ^{o}C under N_2. The stirring was continued for 30 min at 0 ^{o}C and another 30 min at room temperature. Then CuBr (212.2 mg, 1.5 mmol) was added and stirring was continued for 30 min. Next, 2-bromomethylnaphthalene was added and the resulting mixture was refluxed (80 ^{o}C, oil bath) for 5 h. After being cooled to room temperature, the mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give trimethyl(3-(naphthalene-yl)prop-1-yn-1-yl)silane **D** (530 mg, 89%) as a white solid: ^{1}H NMR δ 0.22 (s, 9H), 3.82 (s, 2H), 7.45-7.50 (m, 3H), 7.80-7.84 (m, 4H); ^{13}C NMR δ 0.30, 26.54, 87.36, 104.38, 125.65, 125.75, 126.31, 126.41, 126.50, 126.63, 127.81, 132.47, 133.63, 133.98.

2-(Propa-1,2-dien-1-yl)naphthalene; p5.

The trimethylsilane product **D** (160 mg, 0.67 mmol) was dissolved in THF (5 mL) under N_2. A solution of tetra-*n*-butylammonium fluoride (TBAF) in THF (1 M/THF, 810 µL, 0.81 mmol) was added dropwise and stirring was continued for 30 min at room temperature. During this time, the reaction mixture turned to deep pink color. The mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with Et_2O. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give 2-(propa-1,2-dien-1-yl)naphthalene **p5** (106 mg, 95%) as a white solid: ^{1}H NMR δ 5.23 (d, J = 6.8 Hz, 2H), 6.35 (t, J = 6.8 Hz, 1H), 7.41-7.52 (m, 3H), 7.67 (s, 1H), 7.77-7.81 (m, 3H); ^{13}C NMR δ 79.25, 94.45, 124.71, 124.83, 125.49, 125.60, 126.31, 127.84, 128.42, 131.55, 132.74, 133.82, 210.48.

2-(Prop-2-yn-1-yl)naphthalene; p6.

A stirred solution of trimethylsilane product **D** (190 mg, 0.80 mmol) in EtOH (4 mL) was treated with $AgNO_3$ (0.35 M, 3.5 mL, 1.23 mmol) in EtOH/H_2O (2.3:1). The resulting mixture was covered with aluminum foil and stirred for 2 h at room temperature (a white solid was precipitated during this time). An aqueous solution of NaCN (7.6 M, 1 mL, 7.6 mmol) was then added and stirring was continued until the disappearance of white precipitate. The reaction mixture extracted with Et_2O. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated at reduced pressure. The residue was column chromatographed (*n*-hexane) to give 2-(prop-2-yn-1-yl)naphthalene **p6** (110 mg, 83%) as a white solid: ^{1}H NMR δ 2.26 (t, J = 2.4 Hz, 1H), 3.78 (d, J = 2.0 Hz, 2H), 7.44-7.50 (m, 3H), 7.81-7.84 (m, 4H); ^{13}C NMR δ 25.51, 70.90, 82.03, 125.74, 126.28, 126.36, 126.51, 127.74, 127.81, 128.33, 128.42, 132.50, 133.65.



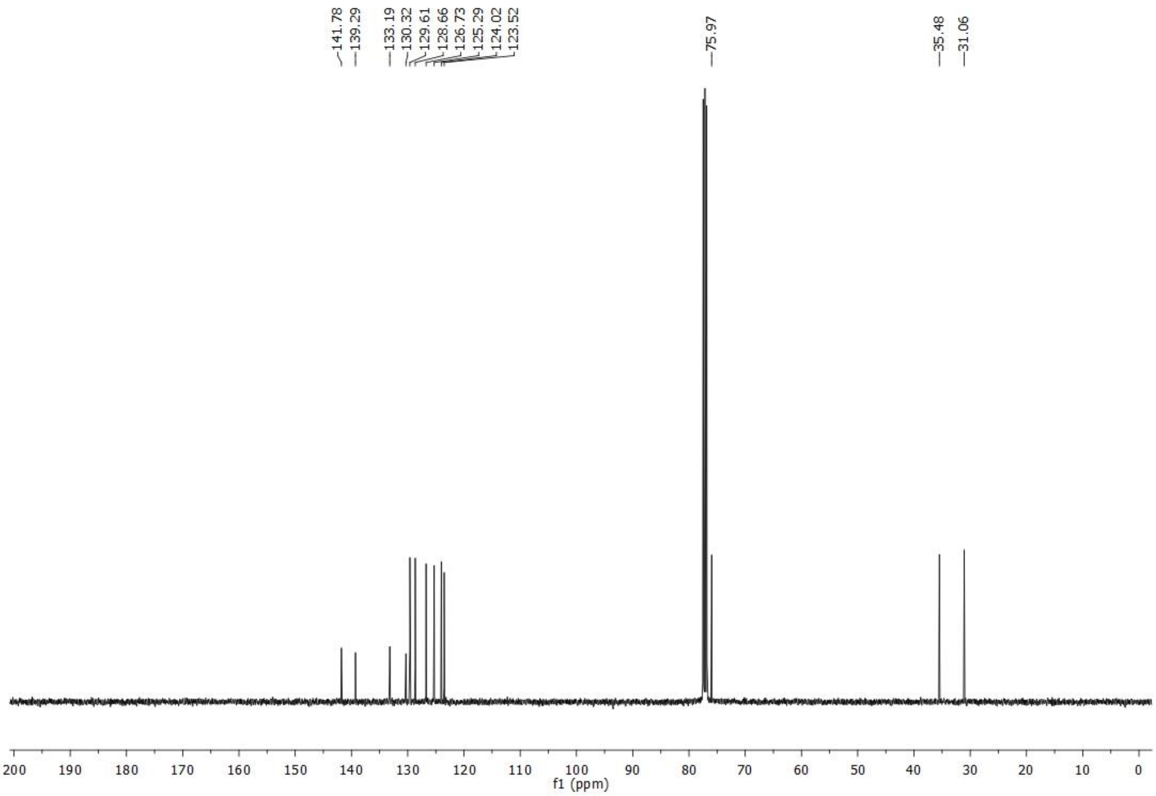
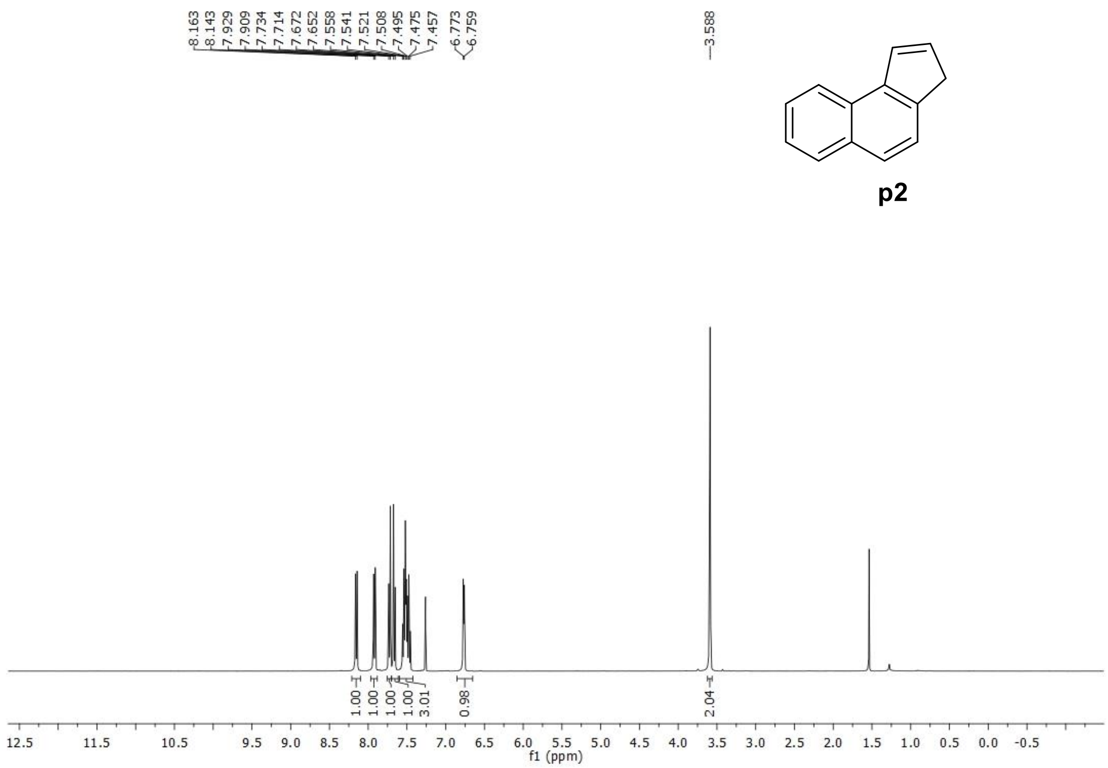


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of compound **A** in $CDCl_3$.



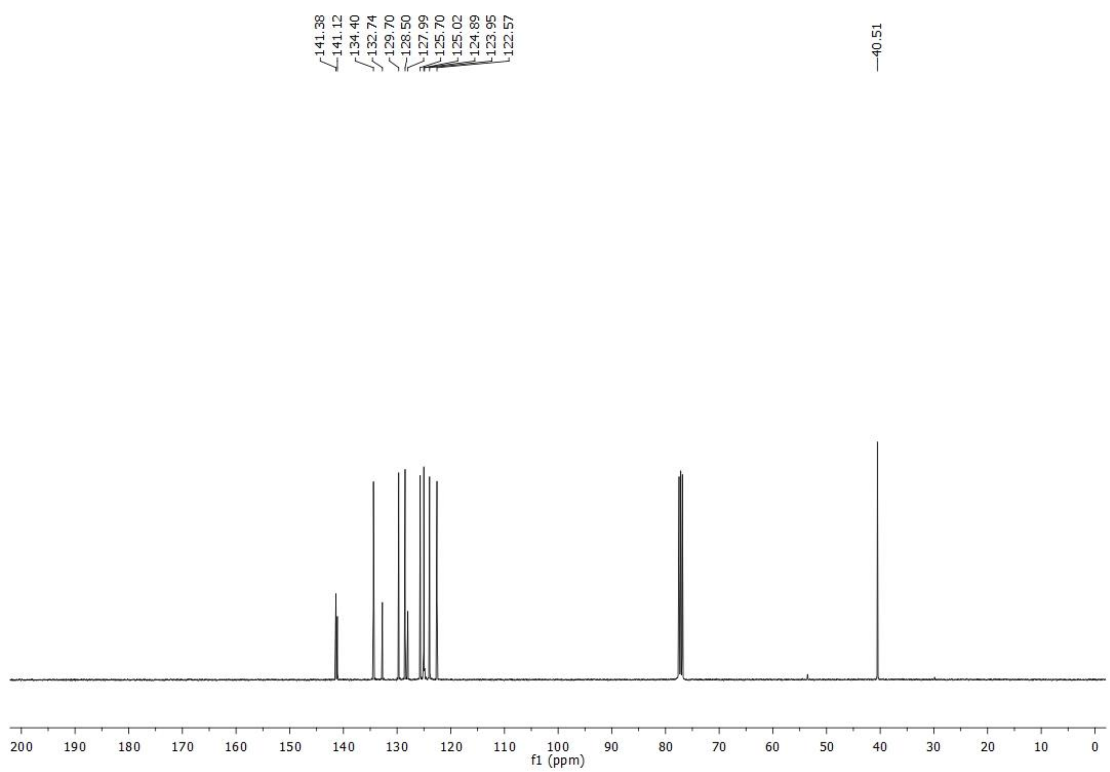


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of compound **p2** in $CDCl_3$.

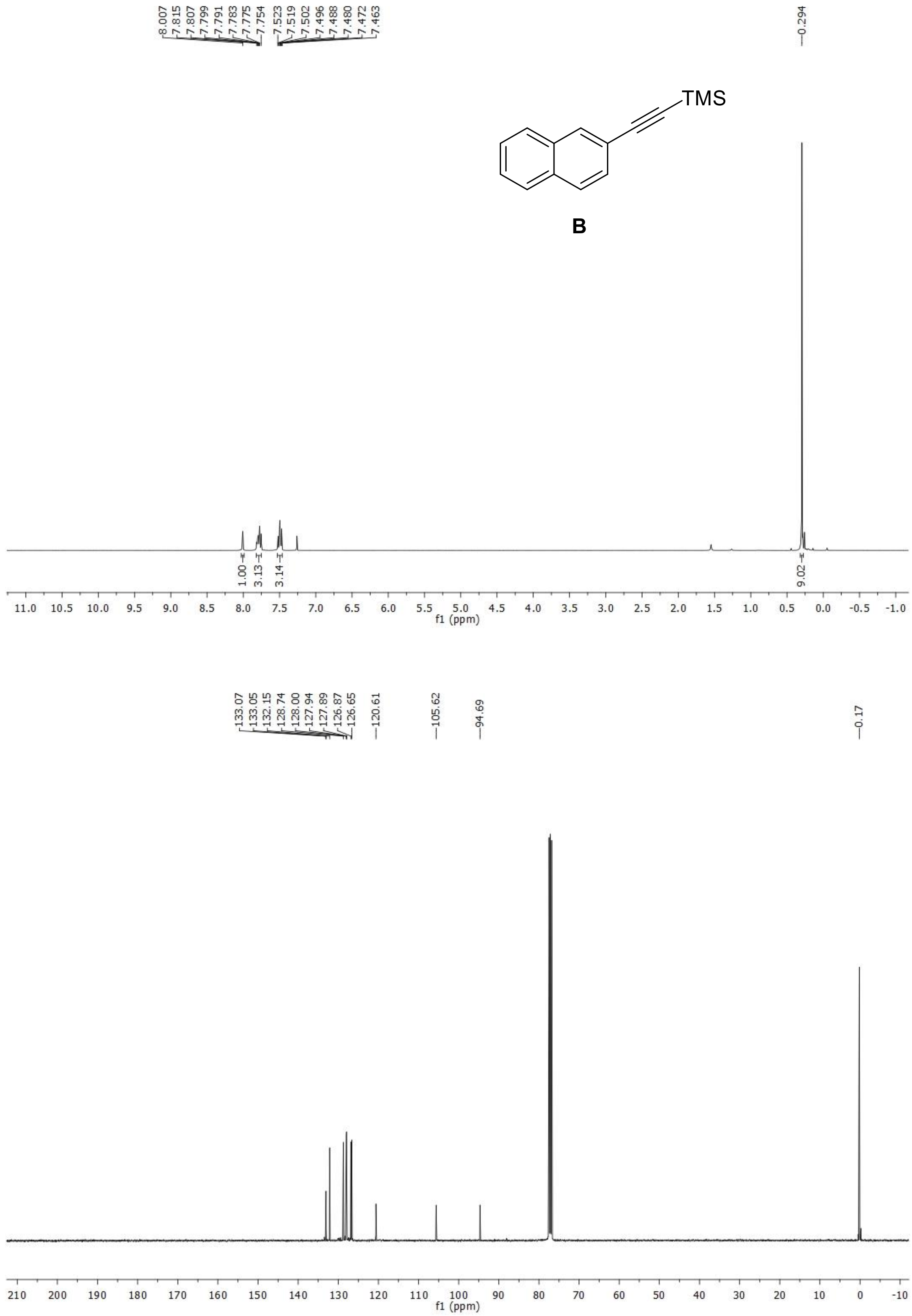
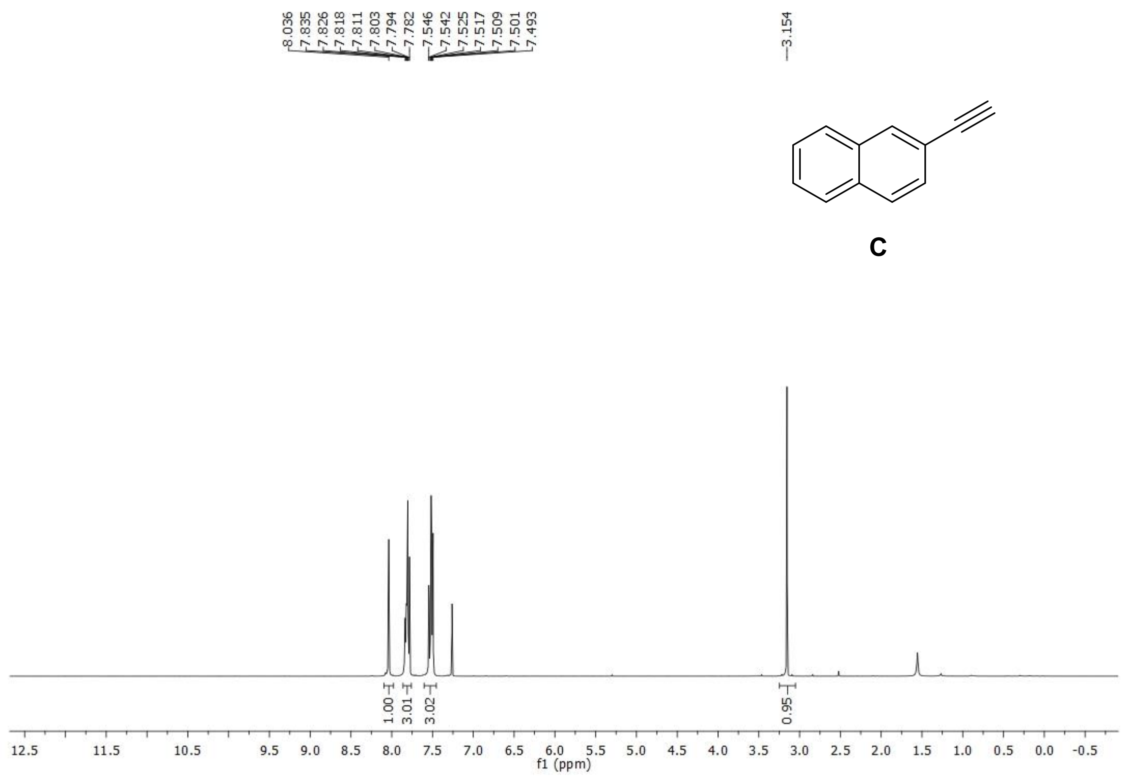


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of compound **B** in $CDCl_3$.



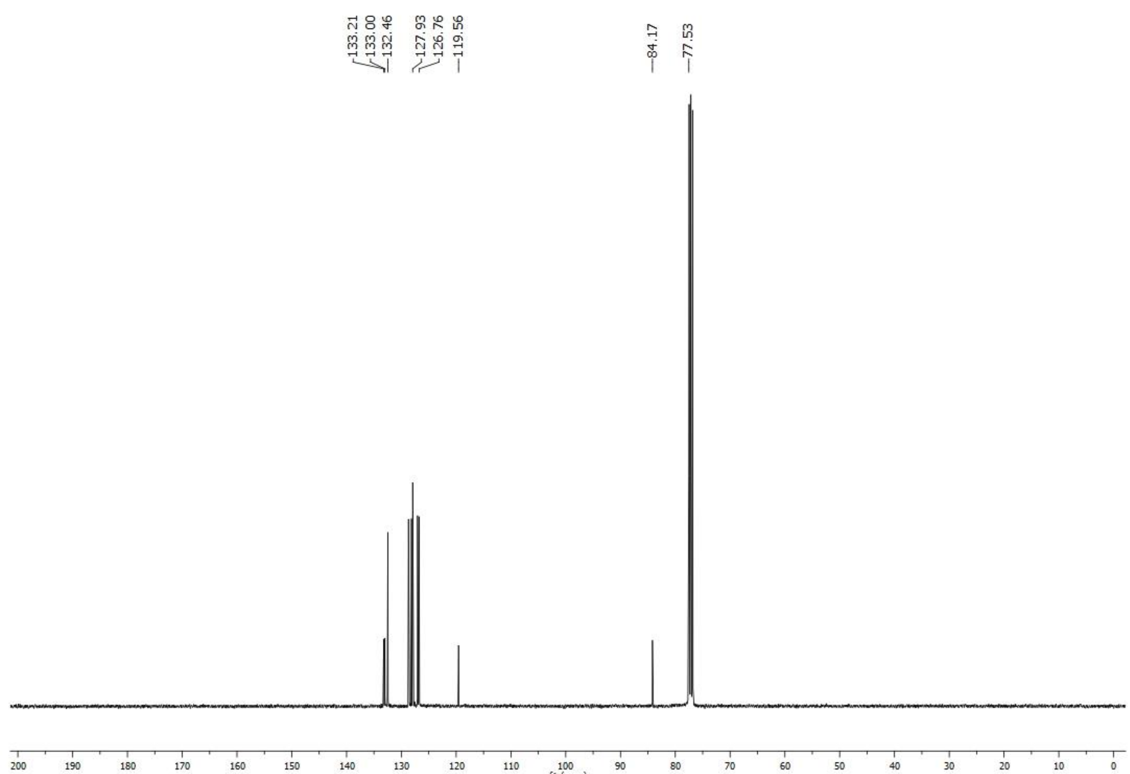
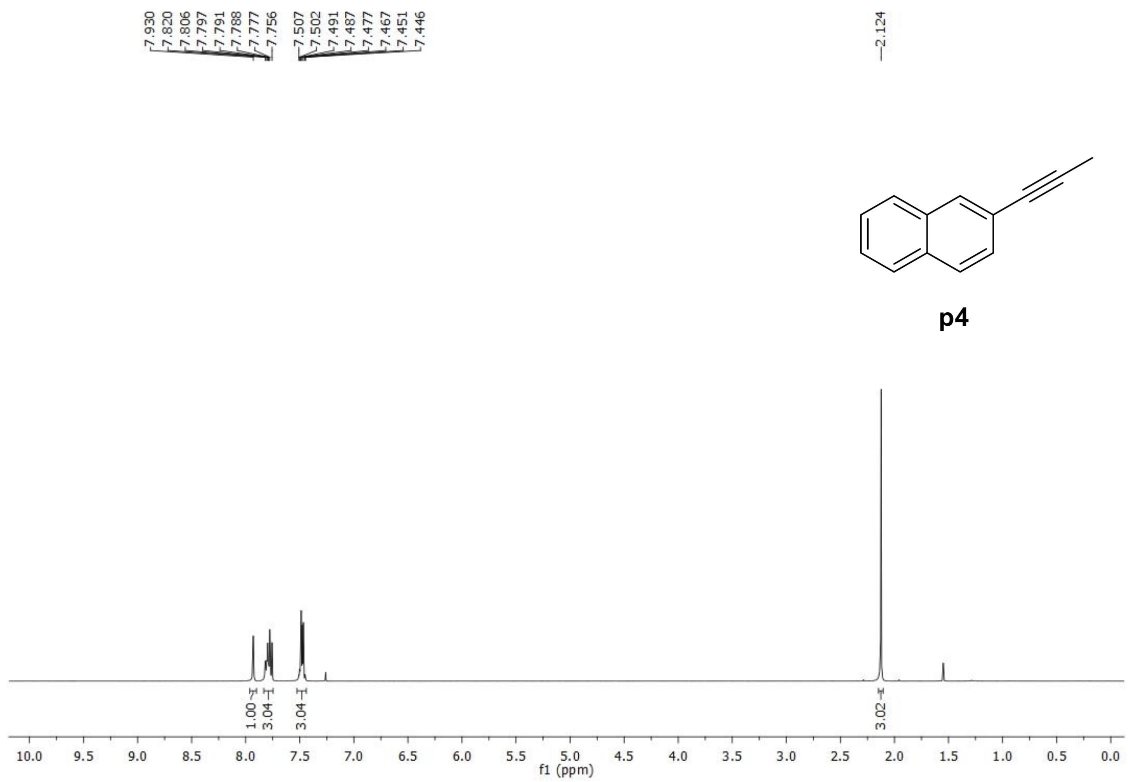


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of compound **C** in $CDCl_3$.



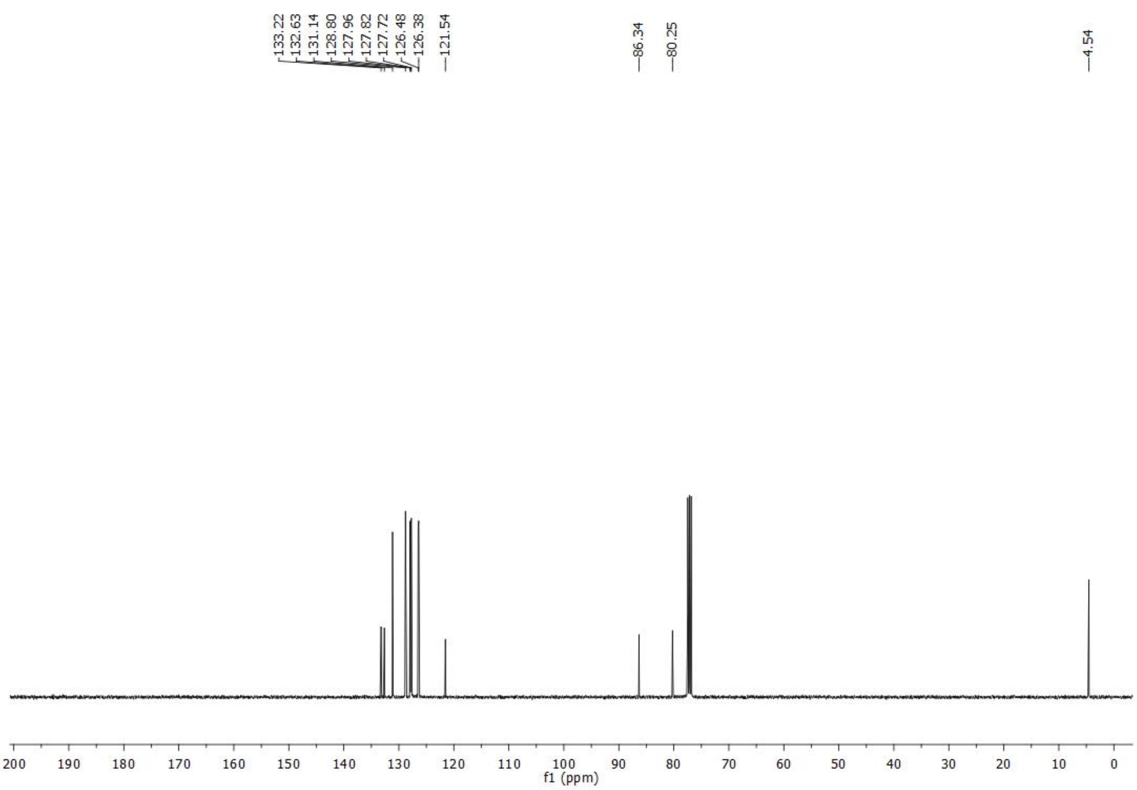


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of compound **p4** in $CDCl_3$.

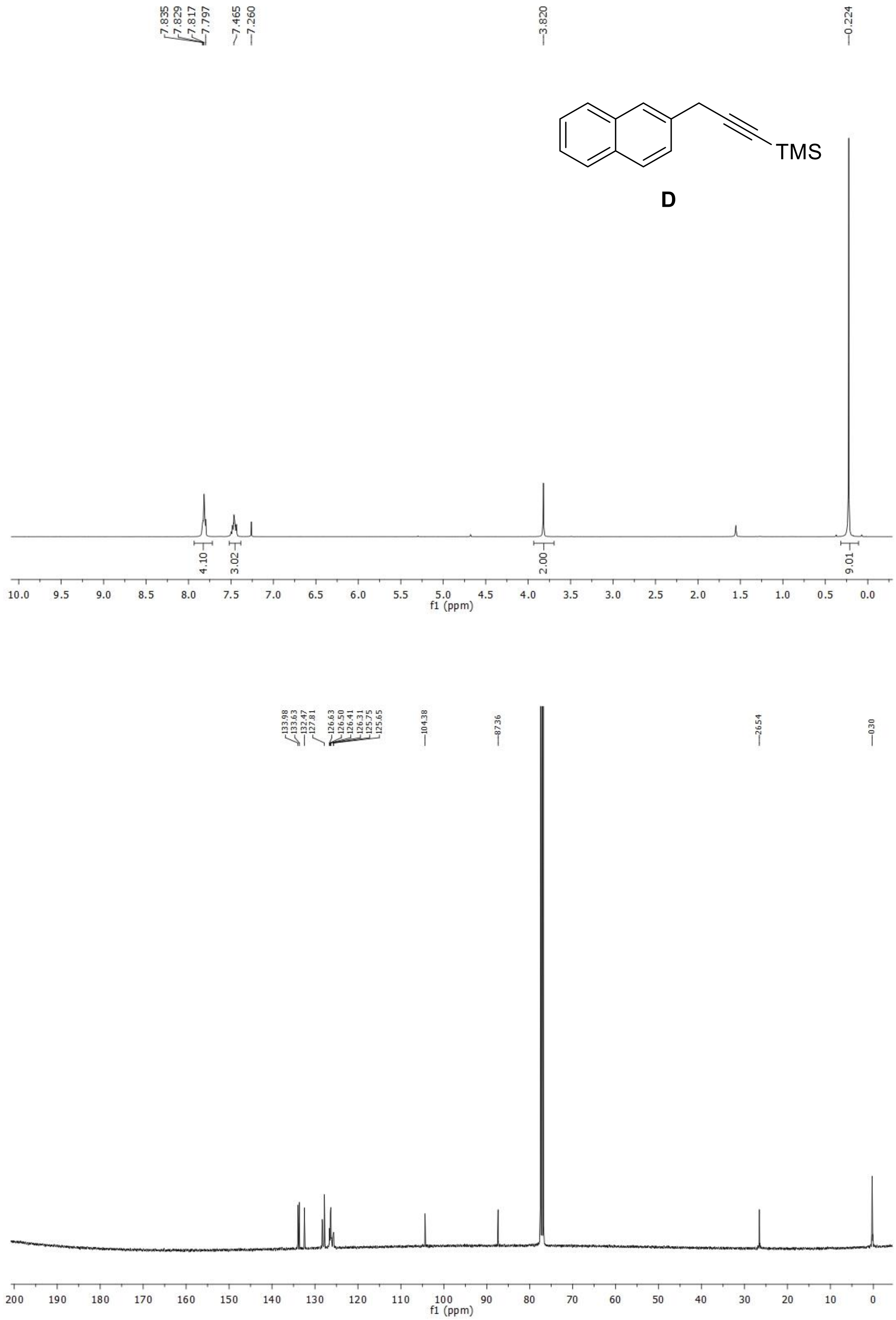
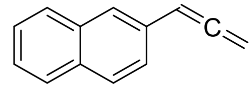
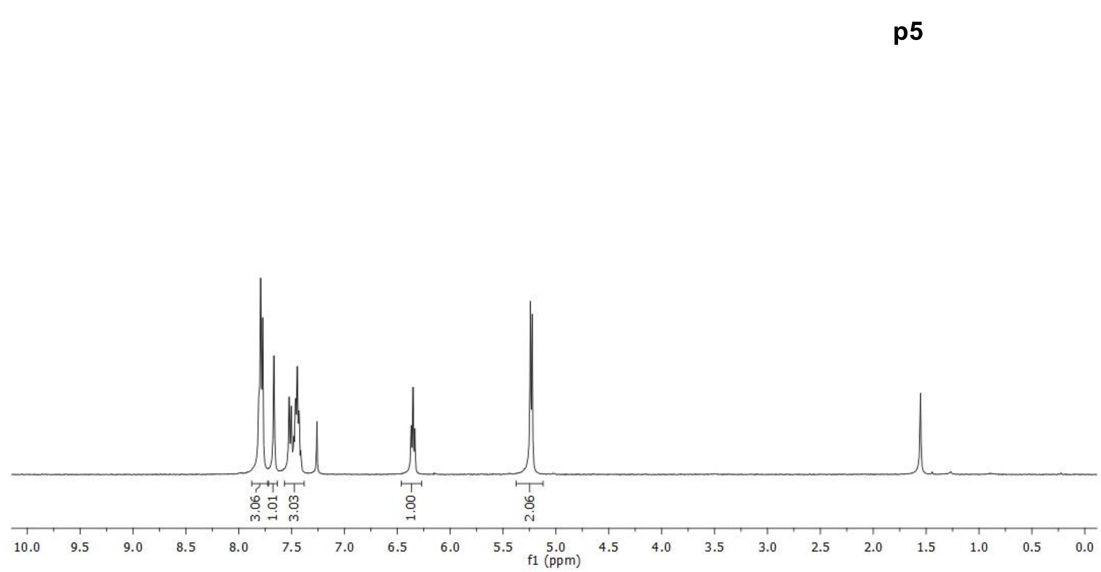


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of compound **D** in $CDCl_3$.



p5



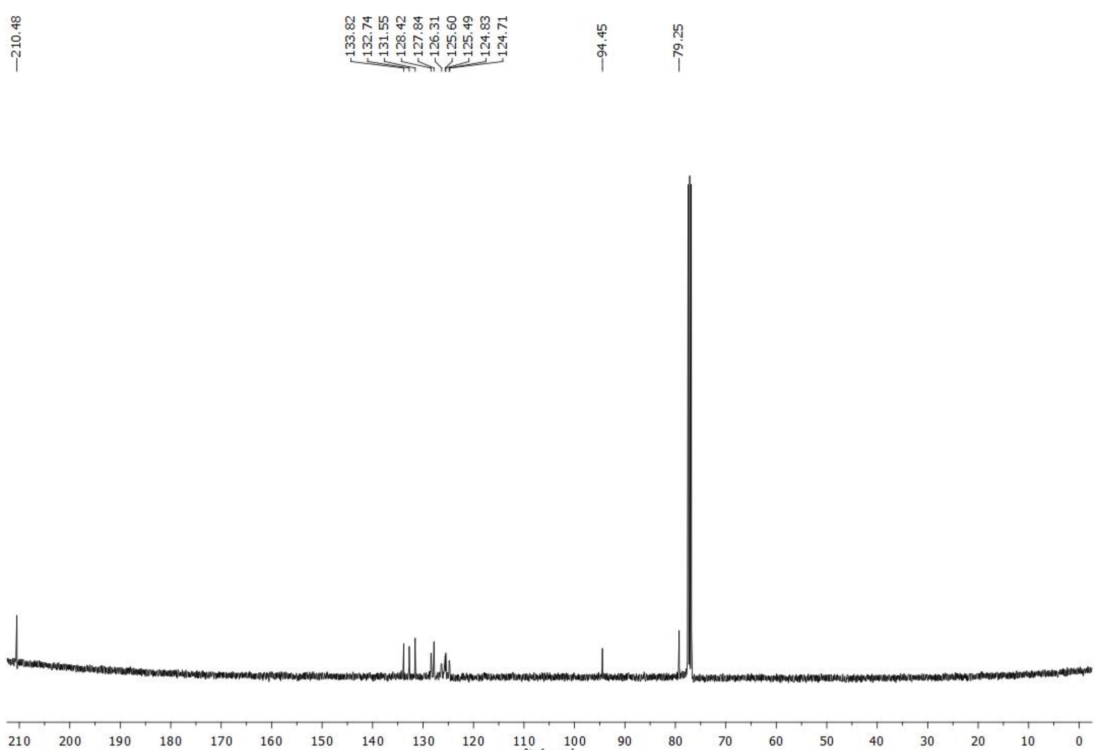


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of compound **p5** in $CDCl_3$.

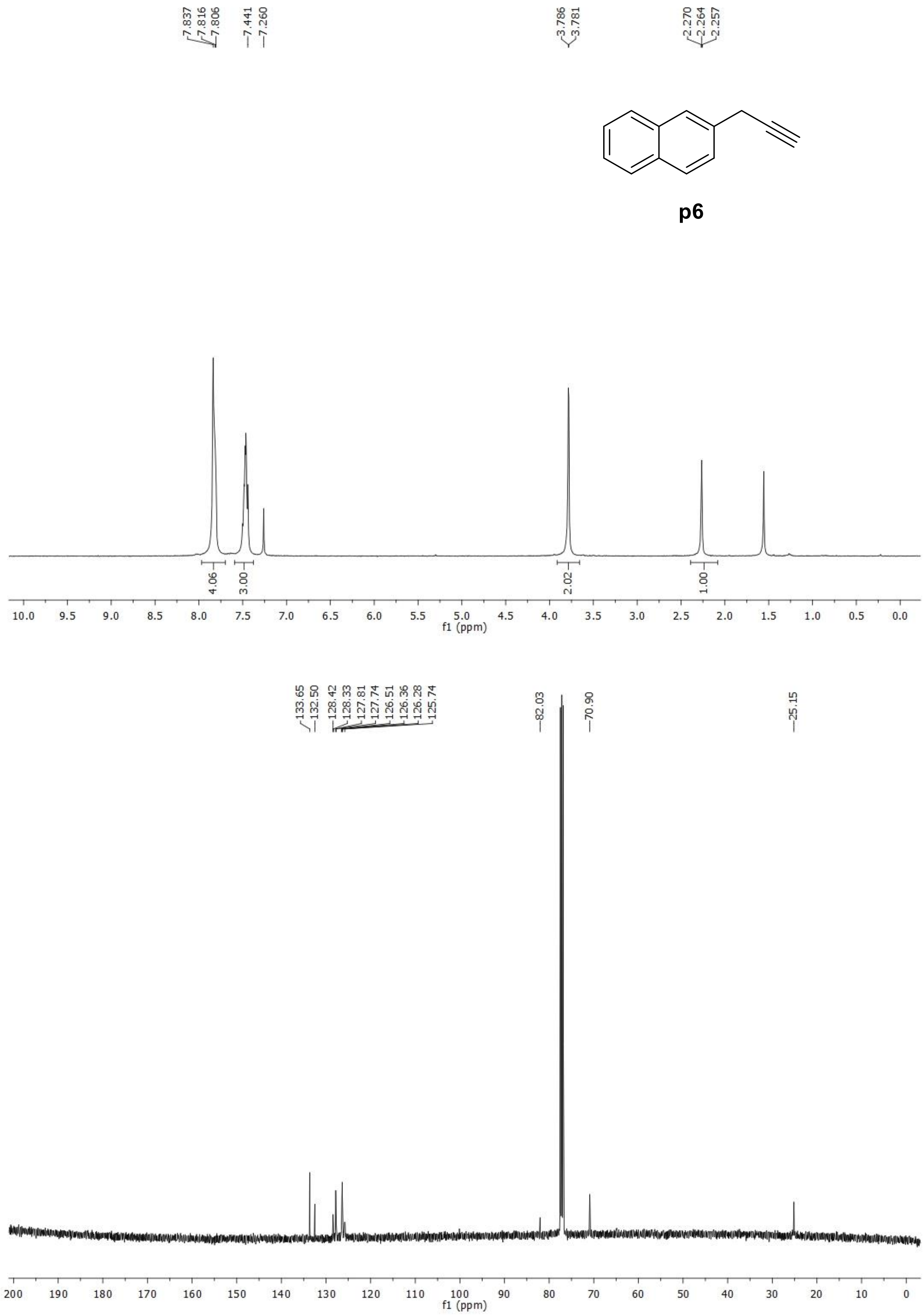


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of compound **p6** in $CDCl_3$.

Input file for RRKM-ME calculations using the MESS package

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1408.9817             1466.2942             1484.3235
1489.5704             1500.0564             1540.2911
1606.7357             1640.4797             1647.5405
1667.2374             3024.2219             3077.0074
3122.7573             3156.6554             3159.6615
3162.3911             3174.7330             3183.1604
3187.3135             3188.1533             3249.1780
ZeroEnergy[kcal/mol] -37.32
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i5------------
Well        i5
Species
RRHO
Geometry[angstrom]   24
C   -3.9077387148 0.6773913178 -0.0905455934
C   -0.1157330663 -1.194551157 -0.15462891
C   -3.8034629132 -0.6967954535 -0.4163876059
C   1.0377973322 -0.4864489743 0.1364697832
C   -0.3120751464 1.5115850361 0.4907242459
C   0.9130447211 0.891646305 0.4680288666
C   -2.7823314 1.4067393009 0.2050695535
C   -2.577428896 -1.3131178029 -0.4400617135
C   -1.4993468667 0.8006455902 0.1888744338
C   -1.3915031252 -0.5878995434 -0.1410284182
H   -4.8828470415 1.1511871366 -0.075436649
H   -0.0417423059 -2.2501089002 -0.3948466904
H   -4.7001208543 -1.2608675678 -0.6474669053
H   -0.3817680912 2.564657098 0.7433214518
H   1.7973240013 1.4700324271 0.703699412
H   -2.8601575431 2.4597880474 0.4554536116
H   -2.4961434741 -2.3659900317 -0.6891995248
C   2.5515754297 -2.3432553558 -0.4287218497
C   2.3709778599 -1.1499521889 0.1042913409
C   3.5632110714 -0.4165653754 0.7070209975
H   3.3741168957 -3.0263141644 -0.5798586853
H   3.3629655842 -0.1376119685 1.7460374489
H   3.7816576607 0.4993770289 0.1493477984
H   4.4554928825 -1.0426408039 0.6854476014
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
21.3639               87.3776              168.0427
181.6143              221.0295              239.9350
310.6918              348.8985              394.6243
450.8998              463.7035              483.6950
504.5956              528.9001              564.0251
627.5050              641.2032              671.5498
672.7411              760.1144              780.5829
```

```
782.1215              829.1879              856.8731
865.1149              873.4814              921.3393
957.8148              963.2429              974.2890
996.1019             1009.3399             1030.2812
1039.7822             1079.2824             1155.2555
1173.6721             1185.6305             1211.0896
1245.7709             1282.0305             1290.6028
1377.1647             1391.1528             1401.1921
1405.2552             1465.6271             1484.3200
1486.3646             1500.7994             1543.2323
1602.9012             1633.5919             1649.5806
1672.5192             3022.0316             3077.6746
3115.4392             3156.5546             3161.0087
3161.9346             3164.8390             3174.8103
3187.2700             3194.0418             3237.5227
ZeroEnergy[kcal/mol] -37.12
ElectronicLevels[1/cm]        1
0  2
End
End
!----------------------------------
!-------well_i6------------
Well        i6
Species
RRHO
Geometry[angstrom]   24
C   -3.6711917155 0.3237348412 0.0146535213
C   0.3296297363 -0.9485507976 0.1032394351
C   -3.3952110283 -1.0608305392 0.1264846896
C   1.4219704157 -0.129863259 0.0323605833
C   -0.1960377272 1.7080570688 -0.1113440887
C   1.1035865176 1.2633462841 -0.0800062813
C   -2.6465483238 1.2352910613 -0.0635352145
C   -2.1002497998 -1.5139020216 0.1585240916
C   -1.2930693069 0.8126609823 -0.0342014643
C   -1.0169243803 -0.5965173273 0.0796364433
H   -4.7008483573 0.6621874026 -0.0090435915
H   -4.216881031 -1.7654168848 0.187031929
H   -0.3977823681 2.770490626 -0.1971908771
H   1.9097486765 1.9846192245 -0.14185622
H   -2.8601471504 2.2958832771 -0.1491889444
H   -1.8819927987 -2.5718136573 0.2439435489
H   2.3005106025 -2.6713794329 0.23600189
C   3.091013656 -1.9324714097 0.1728804469
C   2.8215874396 -0.6251688465 0.0674441829
C   3.9367162663 0.3884073265 -0.0192815744
H   4.1117004246 -2.2954507404 0.198610594
H   3.8859807829 0.9632921655 -0.9499212054
H   4.9075371785 -0.1070822644 0.0174539555
H   3.8925342907 1.1063609206 0.8063971499
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
```

16.8782	84.0209	160.4246
179.5530	228.7675	240.6793
316.6528	336.5418	402.5950
450.2503	477.6864	501.5406
507.1230	522.5373	546.5240
626.3906	632.9779	680.9454
725.1192	760.9675	772.6681
780.9788	826.0563	867.7764
874.5786	923.9828	932.6932
955.7678	963.1212	969.2093
996.8588	1026.3847	1037.0278
1068.4136	1135.7535	1155.6998
1175.4046	1186.8487	1238.6802
1266.1911	1286.1081	1353.5943
1366.7527	1387.5668	1411.1263
1435.6492	1450.3254	1485.3823
1491.3467	1500.5098	1520.6085
1577.2365	1631.7715	1654.6484
1688.9047	3018.7091	3064.9541
3110.8572	3137.2342	3157.1235
3163.7139	3168.7362	3181.0877
3186.4817	3191.4341	3221.4757

```
ZeroEnergy[kcal/mol] -36.45
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i7------------
Well        i7
Species
RRHO
Geometry[angstrom]   24
C   3.6155696094 -0.1105140056 0.0190093877
C   -0.5014845523 0.8638744548 -0.1264613836
C   3.2148322678 1.2317834313 -0.1795161485
C   -1.4656384707 -0.1139073783 0.0113272358
C   0.2836470276 -1.788071777 0.2597047661
C   -1.0470144889 -1.4595786063 0.2062011377
C   2.6738239428 -1.1001716871 0.1639867863
C   1.8814776885 1.5578362258 -0.2281132392
C   1.2887240308 -0.7969376672 0.1176230604
C   0.8823957851 0.5597003729 -0.07970408
H   4.6713830311 -0.3542730487 0.0556010842
H   3.9676634304 2.0037194015 -0.2932799642
H   0.5836003498 -2.8185776427 0.4200256721
H   -1.7989636965 -2.229588406 0.3350151459
H   2.9787842648 -2.1304401022 0.3159337914
H   1.5733454042 2.5869980599 -0.3808280808
C   -3.7792884114 -0.595818933 -0.7752427608
C   -2.9212703888 0.2218569167 -0.0477851862
C   -3.3919115557 1.344493205 0.6242130182
H   -3.4160525017 -1.4474464032 -1.335204311
H   -4.8403819072 -0.3814458461 -0.8194363277
```

```
H   -4.437843164 1.622019224 0.5694096001
H   -2.7404478041 1.9546097758 1.2356517491
H   -0.799667891 1.8927784359 -0.298334953
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
61.5257              83.7845              162.6394
185.2409             221.9911              315.7415
357.6780             392.8183              435.6403
486.3373             493.4387              525.2572
537.1731             545.4619              554.8259
598.2343             632.8777              679.8387
685.1655             761.2647              770.9907
781.7611             785.9993              803.3766
835.9515             875.6318              885.3958
920.2442             964.6880              964.7314
979.9108             982.8435              995.9836
1035.5727            1041.5489            1121.4455
1160.4613            1172.2825            1180.4777
1223.9415            1267.2190            1288.6271
1289.4845            1373.9898            1386.1491
1398.8525            1409.3421            1463.9660
1484.7258            1501.1796            1524.7840
1542.3290            1607.2459            1642.8188
1669.6550            3141.4305            3148.5334
3156.9577            3160.0793            3162.4895
3167.2797            3174.8597            3181.7476
3187.2782            3240.7412            3242.6521
ZeroEnergy[kcal/mol] -60.6
ElectronicLevels[1/cm]       1
0  2
End
End
!-----------------------------------
!-------well_i8------------
Well        i8
Species
RRHO
Geometry[angstrom]   24
C   -3.6069916063 0.0933806358 -0.014399582
C   0.5232274086 -0.8404488152 0.0338217063
C   -3.1899025062 -1.2568891675 -0.0068253034
C   1.4784895278 0.1570933746 0.0423482363
C   -0.2929262425 1.8300884249 0.0189298477
C   1.0371361099 1.5144865183 0.0344967368
C   -2.6760639873 1.1057333976 -0.0061665353
C   -1.8512260393 -1.5692468126 0.0088292287
C   -1.2895990978 0.8158598092 0.00996429
C   -0.8659863833 -0.5481749345 0.017649851
C   3.8491366344 0.8012376427 0.0674349468
C   2.9316624237 -0.1482223866 0.0592883826
C   3.3718327764 -1.6063109785 0.0674458013
H   -4.6655371871 0.3274870649 -0.0267436435
```

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H   0.8171564505 -1.8833483741 0.0393652129
H   -3.9322153279 -2.0471411743 -0.0134284284
H   -0.6054076669 2.8693977329 0.0131960327
H   1.7844344467 2.299791198 0.0411659233
H   -2.9939069739 2.1433117662 -0.0119527367
H   -1.5305682111 -2.6060499414 0.0146519437
H   4.9274036997 0.8586785425 0.0792815085
H   3.0019323615 -2.1281980513 -0.8204528702
H   2.9819598016 -2.1243441365 0.9490296296
H   4.4590835886 -1.6846233349 0.0798918213
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
43.0655             88.5825             166.7133
182.4922            229.0412             242.0227
319.7288            349.1879             396.9751
454.5990            456.4615             486.2481
496.6197            526.9496             566.6385
630.1026            644.7449             673.3770
674.9245            761.2891             782.8811
783.7264            835.7384             859.1722
873.6733            882.1750             906.9230
957.3329            963.6825             985.1207
987.8938            995.7416            1031.7494
1043.1632           1084.3517            1151.8602
1174.4745           1178.8677            1215.9186
1247.1430           1288.6722            1294.3394
1373.8350           1393.7401            1399.5345
1412.8511           1467.2449            1486.3453
1487.3755           1500.7769            1539.7891
1608.0798           1639.9450            1649.1674
1667.8393           3022.9812            3078.6409
3116.4845           3155.6792            3157.9078
3161.2399           3174.0728            3179.3240
3180.8739           3187.4966            3237.4109
ZeroEnergy[kcal/mol] -38.25
ElectronicLevels[1/cm]       1
0  2
End
End
!-----------------------------------
!-------well_i9------------
Well        i9
Species
RRHO
Geometry[angstrom]   24
C   -3.6224535805 0.5374817594 0.0100480652
C   0.2266136829 -1.2130305838 0.0096705889
C   -3.4895000006 -0.8691735627 0.0050148338
C   1.3852976328 -0.4288133917 0.0144288793
C   -0.0224199211 1.5670425176 0.0196320969
C   1.2180035992 0.9979902801 0.0194897513
C   -2.5020873053 1.3394486925 0.0148269549
```

```
C   -2.2432904943 -1.4493120826 0.0048408971
C   -1.2070171246 0.7743088153 0.0147812142
C   -1.0681050083 -0.6505541978 0.0096940827
C   2.6669993235 -1.0646723852 0.0141545649
C   5.1178511815 -1.1130041012 0.0172824154
C   3.9287779547 -0.4413560672 0.0182280034
H   -4.6105737925 0.983382751 0.0101300005
H   0.3223056565 -2.2945379609 0.0058070231
H   -4.3777207126 -1.4909526893 0.0012890767
H   -0.1224811306 2.6477651041 0.0235061236
H   2.092112531 1.6371475835 0.023283836
H   -2.6022398457 2.4200179961 0.0187008956
H   -2.1409804526 -2.5295201029 0.000986898
H   2.6599877602 -2.1520791973 0.010010755
H   6.0641821341 -0.5874439922 0.0201508282
H   5.1524837976 -2.1973141562 0.0137964275
H   3.9668111146 0.6446549716 0.0219097878
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
59.6049              129.6801             133.0886
166.1036              184.7885             309.7656
311.0694              327.2713             402.5542
433.6023              478.3128             524.7586
528.0305              582.4115             602.1255
639.2645              649.7429             755.4975
766.2610              775.0454             778.9246
815.1026              822.4663             849.9191
870.4852              892.0951             896.6836
955.8556              958.9410             973.9116
992.8064              999.8935            1003.2637
1042.5727             1142.5128             1170.8248
1174.9943             1198.7471             1213.2405
1238.6962             1274.4540             1290.5746
1308.6539             1334.1260             1388.0987
1392.5295             1416.2159             1461.5694
1489.7663             1500.2629             1537.2217
1542.1253             1590.1533             1629.9968
1650.4433             3132.5741             3138.5891
3146.7678             3156.2313             3157.9789
3160.1835             3163.3071             3175.3986
3188.2571             3191.9895             3230.7649
ZeroEnergy[kcal/mol] -65.69
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i10------------
Well        i10
Species
RRHO
Geometry[angstrom]   24
```

```
C   -3.6493242995 0.5735470844 -0.1452412478
C   0.1809207835 -1.2019959828 0.079553051
C   -3.5216361778 -0.8333728293 -0.1985002434
C   1.3406804466 -0.4282139952 0.1853955444
C   -0.0596668419 1.5731744203 0.204270295
C   1.1774496942 0.9952579726 0.2662459192
C   -2.5311445483 1.3667699793 -0.0187907227
C   -2.2820470186 -1.4216085918 -0.1246777867
C   -1.240711587 0.7928549858 0.0572170653
C   -1.1076678019 -0.6312806704 0.0035604134
C   2.6121716974 -1.0955864181 0.2487196049
C   4.3509703305 0.6066362315 -0.407460719
C   3.9236128874 -0.5959007033 0.0829132066
H   -4.6330422153 1.0253001321 -0.2040189147
H   0.2712340122 -2.2832308288 0.038002107
H   -4.4092827237 -1.448001286 -0.297792788
H   -0.1566908321 2.6513600344 0.2826448993
H   2.046088422 1.6185423064 0.4251708504
H   -2.6275207971 2.446790116 0.0242682724
H   -2.1835360815 -2.5014318466 -0.1652823162
H   2.5490085545 -2.16270503 0.4431777195
H   5.4106395434 0.8196466966 -0.4758513948
H   3.6783615348 1.3606686303 -0.7923895868
H   4.7049340184 -1.3060974076 0.3476217717
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
49.8806              100.8988              136.5411
188.5402              216.3213              264.2685
333.3133              392.2019              406.7560
419.3030              479.6661              522.8956
528.0985              569.3201              623.4643
639.6441              656.2147              752.6535
760.1797              775.7416              780.5665
792.5792              831.4076              850.2815
871.3939              884.9528              901.7047
958.4768              962.3715              987.0937
992.5674              994.8571             1034.3766
1042.5503             1107.3842             1153.4326
1174.0998             1177.6220             1206.8484
1245.8912             1279.9150             1288.1722
1297.5482             1355.8983             1392.0175
1406.4136             1442.6882             1454.2988
1483.1624             1488.8671             1536.5418
1559.9195             1589.8976             1628.1535
1651.8929             3118.0955             3145.5017
3153.8292             3156.2958             3158.2009
3160.3063             3163.6236             3175.4937
3188.3735             3212.2464             3242.8691
ZeroEnergy[kcal/mol] -62.0
ElectronicLevels[1/cm]        1
0  2
End
```

```
End
!-----------------------------------
!-------well_i11------------
Well        i11
Species
RRHO
Geometry[angstrom]   24
C   3.6489124218 0.5462303942 0.279666327
C   -0.2253820534 -1.176294578 -0.1967710789
C   3.4984420562 -0.8516308353 0.2346061825
C   -1.3049162502 -0.3892283221 -0.3943679749
C   0.1336824125 1.660064152 -0.2709344993
C   -1.1751775015 1.0908781965 -0.6952668057
C   2.5523386477 1.367443927 0.1279441993
C   2.2379882254 -1.4073677017 0.0499155108
C   1.248794483 0.8328980068 -0.0894673394
C   1.1014324422 -0.6058878223 -0.1112722853
C   -2.7232426078 -0.6687318257 -0.260697086
C   -2.509260277 1.6901266267 -0.1676270008
C   -3.4162953648 0.4793982327 -0.1447262979
H   4.6315956843 0.9781046525 0.4335349508
H   -0.3396752158 -2.2410764643 -0.0149442174
H   4.3630023996 -1.4944450668 0.3534179008
H   0.25849285 2.7381414412 -0.2402238959
H   -1.2353859948 1.1786115823 -1.7996515015
H   2.6695280764 2.445853943 0.1586251751
H   2.1213466026 -2.4865459009 0.037506886
H   -3.1426619725 -1.6657253035 -0.2003013665
H   -2.8873300539 2.5051902111 -0.7909769832
H   -2.3846357953 2.0912038271 0.8475475889
H   -4.4857942147 0.5480956275 0.0138176116
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
88.7557              111.4088             221.6221
249.3454              263.2087             371.1532
382.9945              404.5914             442.4998
468.1022              544.6548             560.5294
617.5827              660.3913             680.3771
705.0729              734.4981             744.4632
758.0152              776.1114             793.5343
827.0968              857.7670             891.5433
906.8091              945.0236             948.5227
967.9861              974.8884             984.4600
1023.8964             1042.6206            1098.6760
1120.7635             1138.6980            1147.9340
1162.2393             1175.6791            1202.9893
1244.4230             1252.2983            1281.8236
1284.9774             1318.5806            1339.8018
1367.1966             1382.6140            1403.8226
1451.3332             1483.0098            1499.8606
1555.3529             1599.9997            1616.1923
1661.5229             2851.0055            2997.4510
```

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3062.1087              3150.0163              3154.0831
3155.9141              3159.7789              3173.4004
3180.2784              3187.8540              3202.0502
ZeroEnergy[kcal/mol] -56.18
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i12------------
Well        i12
Species
RRHO
Geometry[angstrom]   24
C   3.7958464732 0.002016814 0.1551284761
C   -0.335209756 -0.8435048613 -0.1687935044
C   3.3546229925 -1.335141674 0.0640714803
C   -1.2945851304 0.2020163812 -0.1896048346
C   0.5227503231 1.8262721716 0.0121930197
C   -0.8063841133 1.5646605101 -0.0921562446
C   2.8790927224 1.0351814552 0.1391539862
C   2.0128468972 -1.620189182 -0.0409053412
C   1.4982261234 0.778098786 0.0324580247
C   1.0437000667 -0.5792230517 -0.0604418117
C   -2.6326989415 -0.0490332179 -0.2936398237
C   -3.9013756404 -0.2811289568 -0.4532963297
C   -4.9113461349 -0.5048382684 0.6524096259
H   4.8553392855 0.2155460661 0.2374818904
H   -0.6765435939 -1.8698182258 -0.2395840618
H   4.0799303168 -2.1410827918 0.0770188481
H   0.8675407771 2.853108177 0.0819526648
H   -1.5306383625 2.3701864706 -0.1064515651
H   3.2160416689 2.0645198702 0.2088617342
H   1.6747100557 -2.6487634924 -0.1110817195
H   -4.4434942211 -0.4503930677 1.6359354096
H   -5.3854318929 -1.4859720993 0.5454053367
H   -5.706649319 0.2460407347 0.6023461393
H   -4.3035465966 -0.3250115478 -1.4709133998
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
43.4020                77.4461               117.3978
143.8946               179.2768               213.0037
261.6343               341.6312               351.2802
399.1634               467.5913               486.6121
510.7458               524.2664               552.5185
627.9539               638.8825               677.8971
751.1375               759.4565               768.1959
773.3555               818.1814               839.1897
871.0952               877.9623               939.1176
953.0870               955.2411               979.1128
987.5019              1042.9277              1054.0182
1066.4858              1123.6996              1158.9187
```

```
1170.9823            1177.3219            1220.1437
1263.2429            1288.4621            1323.3021
1345.9394            1373.0002            1400.4762
1409.9999            1451.5929            1471.3351
1485.2102            1492.3596            1517.6141
1563.9701            1621.3503            1632.9135
1908.4732            3018.4898            3030.1147
3068.4928            3117.0163            3156.3672
3158.9481            3162.0155            3174.7754
3178.2790            3188.4199            3189.4102
ZeroEnergy[kcal/mol] -45.94
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i13------------
Well        i13
Species
RRHO
Geometry[angstrom]   24
C   3.6029795805 -0.1269478816 0.107728744
C   -0.4986047026 0.8190909805 -0.2780256337
C   3.2040079132 1.2081762145 -0.0805987972
C   -1.5338252759 -0.2171523031 -0.2067396262
C   0.2680364828 -1.8758306599 0.0836080401
C   -1.0445957716 -1.6002345685 -0.03169383
C   2.6439119896 -1.1329028773 0.1627618451
C   1.8687447557 1.5276286926 -0.2092203153
C   1.2823254272 -0.8438296835 0.0363930577
C   0.8629250269 0.5199561436 -0.1531969
H   4.6541220248 -0.3707866466 0.207807106
H   -0.811314682 1.8457408001 -0.4360746031
H   3.9525152017 1.9917147259 -0.1251291191
H   0.5944788765 -2.9030813786 0.2135501971
H   -1.7832100057 -2.3943596903 -0.0030686509
H   2.9497925334 -2.1646758189 0.3053099105
H   1.5646459273 2.5590706404 -0.3540673282
C   -3.4112884385 0.0332181973 -2.1037522386
C   -2.8301644552 -0.0001759359 -0.9214705655
C   -2.911122135 0.1540537564 0.5166084087
H   -2.8522750089 -0.1701877203 -3.0108056065
H   -4.4671248147 0.2649436354 -2.206583905
H   -3.3558239582 -0.6343452663 1.1168790595
H   -2.9684244912 1.1494996443 0.9466957506
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
53.4873              92.6295             177.3986
182.7825             233.7767             280.2562
362.8145             372.6432             412.2195
442.0220             466.4859             502.4190
510.5536             547.3933             617.3095
```

```
648.3904               668.9138               689.9380
719.1838               750.2947               757.7492
779.7213               801.5927               849.3599
863.9052               893.3926               921.5139
927.8405               933.0050               939.7836
974.4720               982.1289              1017.4368
1026.5969              1043.7682              1078.7331
1121.8761              1146.3172              1166.0118
1171.2531              1208.6799              1254.2587
1293.2818              1318.0808              1345.2619
1414.7238              1425.9777              1437.6208
1459.4771              1465.3239              1506.0680
1560.1938              1608.6869              1651.9473
1817.8471              3094.7741              3120.4536
3151.6867              3155.4207              3159.3249
3166.2944              3173.8913              3174.2490
3181.5657              3188.6372              3204.0166
ZeroEnergy[kcal/mol] -25.7
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i14------------
Well        i14
Species
RRHO
Geometry[angstrom]   24
C   -2.1708788549 -0.9260967149 -0.3726883959
C   1.0893593865 1.6631920972 0.4039510152
C   -2.4095324054 0.429497517 -0.04822489
C   2.3823548735 1.1992362363 0.3447741261
C   1.5648182311 -1.0121357589 -0.2392953773
C   2.6110617828 -0.1625122941 0.0134201264
C   -0.8849899129 -1.4061850374 -0.4371938672
C   -1.3588532039 1.2779392342 0.2054928637
C   0.2213700651 -0.556428538 -0.1807569801
C   -0.0191870874 0.8138277575 0.1475376935
H   -3.0086640883 -1.585144026 -0.5707759611
H   0.8975361375 2.7029599906 0.65215143
H   -3.4284324362 0.7971739777 -0.0006126874
H   1.7542526675 -2.0505915347 -0.491121139
H   3.6315121077 -0.5249128491 -0.0474037239
H   -0.6988288669 -2.4458287662 -0.6863204474
H   -1.5418755997 2.3182701253 0.4541486208
C   3.5587054705 2.1136065638 0.6502071931
C   5.8446403113 1.9199410102 -0.6014353623
C   4.5744444236 2.1773205664 -0.4187825047
H   3.1846346811 3.1215119617 0.8583038611
H   4.0529764614 1.7719585207 1.5773791701
H   6.4706545243 1.5275977338 0.2068777162
H   6.3419573316 2.0842372269 -1.5535534798
Core  RigidRotor
SymmetryFactor  0.5
```

End
Frequencies[1/cm] 66

23.5293	71.2218	106.2674
179.2895	197.7096	241.6284
306.8364	324.0052	403.2800
406.3950	447.4936	487.0145
514.1745	526.7582	581.2887
636.3853	658.5397	735.8589
763.9667	781.1979	786.6345
832.6449	864.3947	878.5778
883.7540	889.7888	913.4227
947.6315	963.8884	977.5358
979.6539	996.2394	1042.1791
1042.5549	1147.5463	1172.2849
1177.9235	1188.0492	1204.4470
1237.0804	1277.1098	1288.2727
1303.1735	1391.7054	1396.5431
1406.7277	1413.4844	1447.3755
1474.0169	1502.4998	1545.8055
1612.3082	1645.6789	1673.1690
1734.1983	2923.2560	3025.6637
3044.3966	3148.0055	3152.9757
3157.0511	3158.8097	3162.5382
3174.7730	3178.2433	3187.6229

ZeroEnergy[kcal/mol] -36.53
ElectronicLevels[1/cm] 1
0 2
End
End
!----------------------------------
!-------well_i15------------
Well i15
Species
RRHO
Geometry[angstrom] 24
C -3.6853081126 0.3132365987 0.1702103376
C 0.3608289559 -0.8464602687 -0.331969764
C -3.3694510029 -1.0152460623 -0.1960618228
C 1.3966585044 0.0491667037 -0.14136726
C -0.2546159212 1.8011835045 0.3969886337
C 1.005369486 1.3450591001 0.2165516366
C -2.6855099659 1.2359034637 0.3652824467
C -2.0597060833 -1.3964940546 -0.3597603906
C -1.3247278148 0.8732493513 0.2031617884
C -1.0000621699 -0.4714203142 -0.1676652918
C 2.8527805263 -0.3334369186 -0.3291945064
C 3.9744330945 -0.6029692777 -2.5658237144
C 3.4180528077 0.1662710387 -1.6360944049
H -4.7226549234 0.6021367903 0.2969927092
H 0.5871443192 -1.8713395262 -0.6141663866
H -4.1673864743 -1.7333902279 -0.3472912581
H -0.4728050859 2.8260688121 0.680144627
H -2.9258272111 2.2558780549 0.6463617595
H -1.8173984251 -2.4161315094 -0.6407623727

```
H   3.4330494535 0.091660233 0.4985215128
H   2.9570784298 -1.4202179574 -0.2727942107
H   4.0594557285 -1.6784160801 -2.4402428471
H   4.3673190168 -0.1865484719 -3.4864509305
H   3.3445228682 1.2394080179 -1.7995902909
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
23.6820               59.0243               101.6365
181.5633              191.6930              248.0398
317.3843              372.9903              397.9920
411.1026              476.6877              480.2778
530.8658              541.4642              617.4221
633.9593              657.9506              746.8350
762.7680              766.9880              777.8534
838.1710              870.9931              875.9615
894.8381              935.2553              940.2048
949.8672              954.7086              964.7459
994.1871             1032.2668             1041.9649
1106.3999             1148.5986             1169.3863
1180.3087             1217.6022             1222.1123
1253.9220             1275.1993             1310.5901
1325.9500             1342.1294             1387.3455
1399.3607             1432.6102             1453.6459
1473.9690             1479.0407             1528.4245
1595.7633             1626.4345             1655.7364
1705.8503             3015.9238             3072.6714
3123.8773             3134.8424             3144.8492
3157.3214             3158.6700             3163.8622
3175.8249             3188.2097             3209.2217
ZeroEnergy[kcal/mol] -32.01
ElectronicLevels[1/cm]        1
0  2
End
End
!----------------------------------
!-------well_i16------------
Well        i16
Species
RRHO
Geometry[angstrom]   24
C   -3.7134868502 0.4626528905 0.2739172892
C   0.214288241 -1.0043733187 -0.0577859539
C   -3.494811008 -0.9322214027 0.3574026028
C   1.3142881011 -0.2303580259 -0.2438987554
C   -0.20765562 1.6827450688 -0.2205981714
C   1.0628592481 1.1754979655 -0.3286915892
C   -2.6583811093 1.3234110898 0.0870521733
C   -2.2252660656 -1.4470199529 0.2526507402
C   -1.3319692981 0.835237156 -0.0255415656
C   -1.1155562205 -0.5842220609 0.0596164515
H   -4.7219473444 0.851509706 0.3586365615
H   -4.3380476807 -1.5973856008 0.5053309714
```

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H   -0.3701676676 2.7532198088 -0.2890533193
H   1.9037839135 1.8457739559 -0.4828550945
H   -2.8279753478 2.3935127984 0.0230310287
H   -2.0501141594 -2.514519772 0.3160451783
H   2.3223365968 -2.4955322298 -1.654109045
C   2.7280854243 -0.7750165058 -0.3358122069
C   3.3978033994 -3.1730374526 0.0059400542
C   2.8010804537 -2.2288520731 -0.7140786691
H   3.276661245 -0.1786533269 -1.0765969219
H   3.2394342126 -0.6177228668 0.6213419624
H   3.8776145937 -2.9485565711 0.9539739199
H   3.4273659427 -4.20543428 -0.3236126411
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
29.4750               63.7939               98.6585
154.7319              180.3027              259.2692
303.6574              371.7089              408.3747
432.7212              474.9463              502.2206
509.5688              520.0494              613.6675
626.7124              648.4669              742.2549
755.5953              771.3618              779.8885
815.5489              875.6975              903.4153
928.6905              943.7640              951.9850
958.1390              969.3808              974.3603
997.1942             1029.9790             1039.7471
1127.6701             1139.4412             1161.7711
1171.0638             1195.6947             1236.1080
1245.6112             1265.1242             1311.1170
1325.8133             1359.6068             1364.7015
1394.7834             1447.4229             1450.8237
1471.1123             1496.4028             1520.5586
1583.0241             1643.1138             1664.7373
1709.9389             3001.8781             3033.6926
3124.0430             3133.4331             3146.7504
3157.4233             3168.5484             3172.1509
3181.6314             3191.7745             3209.6418
ZeroEnergy[kcal/mol] -31.49
ElectronicLevels[1/cm]        1
0  2
End
End
!----------------------------------
!-------well_i17------------
Well        i17
Species
RRHO
Geometry[angstrom]   24
C   3.7558777361 -0.0540624488 0.3680328436
C   -0.3416996382 -0.7685246127 -0.4463485298
C   3.3030906976 -1.3720213857 0.1260750898
C   -1.216707186 0.2870671651 -0.4720146886
C   0.5608043689 1.8583828 0.0358069038
```

```
C   -0.7618178876 1.611174834 -0.2290842351
C   2.8721260868 0.9971502426 0.3402203165
C   1.9763841959 -1.6101524827 -0.1384665874
C   1.4941543391 0.7879163108 0.0701566683
C   1.0352441678 -0.5478781782 -0.1750846005
C   -2.7093623931 0.2752732546 -0.7383053172
C   -1.9121632934 2.59519271 -0.3129352415
C   -3.0893650794 1.7217014013 -0.6289583335
H   4.8052619337 0.1227704547 0.5758652948
H   -0.6837840657 -1.7825540832 -0.6313961324
H   4.009143534 -2.1945588955 0.1504175309
H   0.9140986772 2.8683126525 0.2222260121
H   3.2183818029 2.0088651526 0.525735636
H   1.6277763572 -2.6210058112 -0.32427399
H   -2.9431969492 -0.1491363648 -1.727291071
H   -3.2470865904 -0.3582004996 -0.0155048744
H   -1.7366498704 3.3620844441 -1.0836504992
H   -2.0408605404 3.152806685 0.6280032609
H   -4.0973234032 2.0920946549 -0.7594894562
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
94.3256              122.3123              152.5677
256.8166              258.4568              286.3775
366.4610              404.7816              405.2049
411.6028              486.6988              535.1487
575.3483              629.0985              649.8059
718.4084              724.6065              756.7602
779.4559              785.5189              829.0436
858.7876              869.9437              889.3510
912.8743              920.9225              929.0231
942.2427              965.1186              992.4063
1025.1768             1042.2542             1088.4897
1133.7233             1134.6911             1168.5879
1172.1536             1181.5257             1222.9891
1245.4172             1265.9690             1283.2206
1308.2046             1349.1397             1368.7828
1392.9369             1418.0195             1455.5254
1459.8124             1485.0784             1487.7814
1537.5065             1614.4639             1652.0068
1678.1141             2954.9278             2958.3026
2959.3328             2959.3826             3152.4401
3154.2132             3155.7817             3160.5562
3173.3421             3186.4986             3204.3097
ZeroEnergy[kcal/mol] -65.35
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i18------------
Well        i18
Species
```

```
RRHO
Geometry[angstrom]   24
C   -3.607062069 -0.4605740743 -0.0318252876
C   0.6292210744 -0.3906776281 0.0277618079
C   -2.8882487414 -1.6773337816 -0.046284512
C   1.2868335286 0.8210121746 0.0610070201
C   -0.805030168 2.0109928583 0.0561101079
C   0.5683326982 2.036618594 0.0754479664
C   -2.9353082483 0.7377778544 0.0013687349
C   -1.5135397761 -1.6733497794 -0.0272977677
C   -1.5174417576 0.7812486353 0.0217280292
C   -0.7887686853 -0.4535965745 0.0070463758
C   2.7894119791 0.6349755857 0.0776853037
C   1.6080635607 -1.5476234172 0.0179128255
C   2.9386691442 -0.8562776438 0.0494437806
H   -4.6910512064 -0.4770673972 -0.0470524222
H   -3.4275925484 -2.617699124 -0.072494086
H   -1.369888888 2.9374094166 0.0668786518
H   1.0981762608 2.9832118707 0.1016345141
H   -3.4852400794 1.6733450155 0.0125482626
H   -0.9695478063 -2.6110225926 -0.0385263585
H   3.2723483421 1.1276919034 -0.7815371326
H   3.2485491479 1.0920899577 0.9690463158
H   1.4599913509 -2.2199256023 0.87850768
H   1.4834254148 -2.1853272914 -0.8721972472
H   3.8892594724 -1.3724059599 0.0520514372
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
107.0698              128.5708              178.4724
225.9664              235.7410              276.7820
353.3120              420.6603              428.3135
460.9729              507.0879              519.1917
533.6427              603.8140              642.7945
671.0885              744.3922              751.3863
781.2880              788.6778              819.8450
868.7788              873.0729              911.2819
928.9227              930.0882              958.7208
960.1594              970.2790              993.5074
1025.4853             1045.3607             1072.8194
1129.5222             1137.3259             1167.6873
1177.4641             1184.1963             1212.0690
1234.2226             1271.5683             1283.4381
1324.5049             1346.0158             1377.9853
1400.1540             1412.7110             1457.5895
1463.8005             1470.8255             1497.5447
1552.7075             1612.0443             1636.1373
1665.6815             2948.0004             2950.1224
2952.4369             2952.5572             3155.2200
3157.3450             3165.1983             3173.9764
3178.2905             3188.1393             3204.5390
ZeroEnergy[kcal/mol] -66.0
ElectronicLevels[1/cm]       1
```

```
0  2
End
End
!------------------------------------
!-------well_i19------------
Well        i19
Species
RRHO
Geometry[angstrom]   24
C   3.6318810329 0.4807542745 0.0164837667
C   -0.2434383243 -1.2107040763 0.1715009654
C   3.4731057942 -0.897396964 0.2869243159
C   -1.3837031239 -0.4316568618 -0.0393356273
C   0.0552111971 1.5277580953 -0.330193233
C   -1.1903361535 0.9723244628 -0.2716870932
C   2.5285366997 1.2777531678 -0.1910255182
C   2.2177639331 -1.4537653676 0.3414043115
C   1.2231825373 0.7358196657 -0.1410187339
C   1.0581642944 -0.660774276 0.1251246419
H   4.6272643362 0.9083445479 -0.0243518639
H   -0.3439809883 -2.2578012139 0.424775612
H   4.3486207288 -1.5151830757 0.4522842615
H   0.1703771649 2.5900976259 -0.5195887297
H   -2.066656421 1.5949285609 -0.4185021695
H   2.6483304895 2.3369353075 -0.3945287055
H   2.0951971186 -2.5116851041 0.5493027687
C   -2.7325403717 -0.9266761192 0.0003385113
C   -2.5849411392 -3.3960708672 -0.4579690801
C   -3.2260580323 -2.2484996023 -0.0851142619
H   -3.4928412555 -0.1568802084 0.1001777134
H   -3.1214040518 -4.3366536794 -0.4808369014
H   -1.5578416823 -3.4130030955 -0.7959543381
H   -4.2868677829 -2.3439631969 0.1390253873
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
58.9015              101.5076              129.9387
189.0148              215.3316              278.4754
332.1181              389.6537              410.0791
432.0402              481.8984              523.5196
526.6313              569.6826              605.0500
646.2998              656.8319              739.4751
751.9518              773.1264              779.2752
794.0026              833.6479              854.9327
873.1235              906.7269              924.4219
961.5779              965.1367              978.2899
991.8832              993.5742             1020.8295
1042.5393             1112.0085             1153.8579
1171.0841             1179.3984             1211.4510
1229.4784             1267.6219             1286.0095
1293.7944             1367.4051             1389.9154
1411.1832             1442.4774             1453.8730
1478.7488             1489.1216             1534.9779
```

```
1561.9633              1592.1557              1632.4830
1651.8740              3119.1245              3145.6842
3154.2215              3155.9985              3157.5469
3161.9987              3174.4123              3175.3508
3187.9911              3197.8435              3243.0872
ZeroEnergy[kcal/mol] -62.2
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------well_i20------------
Well        i20
Species
RRHO
Geometry[angstrom]   24
C   3.6230700817 0.4619957723 -0.0842389153
C   -0.3031069253 -1.2250619843 0.5110391305
C   3.4846128781 -0.9173547634 0.0738051482
C   -1.4265864514 -0.345334985 0.002846485
C   0.0309431114 1.564962644 -0.0513082859
C   -1.2438720213 1.0249336922 -0.1416123886
C   2.4972689638 1.2729330543 -0.0993943822
C   2.2137579479 -1.4728422414 0.2311596715
C   1.205775024 0.7294117857 0.0451732
C   1.0745113243 -0.6742348158 0.2252395833
C   -2.5378683456 -1.184410105 -0.3056176019
C   -0.6972323073 -2.6447765608 0.0209552627
C   -2.171488828 -2.4938495309 -0.2745764711
H   4.6079761391 0.9004444951 -0.2002591312
H   -0.4108451995 -1.2340230922 1.6114296777
H   4.3598001422 -1.5570681438 0.0808093914
H   0.1760726786 2.6330330374 -0.1708482773
H   -2.0855113347 1.6644272303 -0.3897136437
H   2.6027307471 2.3442710184 -0.2374252175
H   2.11440712 -2.544390969 0.3699087987
H   -3.5226658597 -0.8182249332 -0.5708291764
H   -0.4824639782 -3.4278222972 0.7536584406
H   -0.1496975418 -2.9074488569 -0.8955033665
H   -2.8191913655 -3.3310424509 -0.5025069317
Core  RigidRotor
SymmetryFactor  0.5
End
Frequencies[1/cm]  66
95.7042               110.4329               211.0156
234.1449               251.2703               394.0126
415.9914               425.1121               437.8193
504.0759               519.7746               539.3193
604.9982               654.0605               690.8255
716.1939               724.9124               750.4712
775.3882               796.1987               814.4065
859.2284               880.9569               921.4952
924.5328               946.7092               948.3532
952.4561               979.6145               983.2397
```

```
1024.6200              1058.9219              1095.7327
1118.8624              1139.2165              1159.6583
1180.5462              1216.7607              1227.0960
1238.9974              1247.5655              1282.7061
1298.3331              1315.9616              1321.0889
1345.9526              1387.8781              1407.0705
1463.7064              1481.3539              1511.7609
1531.3195              1551.4635              1600.2444
1630.8057              2899.7681              2988.1683
3058.2107              3152.5933              3155.1394
3160.4981              3172.3421              3174.9839
3181.3335              3186.8673              3203.2937
ZeroEnergy[kcal/mol] -64.72
ElectronicLevels[1/cm]        1
0  2
End
End
!-----------------------------------
!-------c10h7_c3h4_p0p------------
Bimolecular   p0p
Fragment        c3h4
RRHO
Geometry[angstrom]   7
C   -0.823420841 0.0519880348 -0.0208571707
C   1.824711204 -0.1816552298 0.0001678957
H   -1.8820502847 0.1362504236 -0.0342313517
H   2.1265806386 -1.2327357481 0.0038417281
H   2.2515118512 0.2935470245 0.887798287
H   2.2667123243 0.2920674571 -0.8807572055
C   0.3727611076 -0.0556769621 -0.0121801829
Core  RigidRotor
SymmetryFactor 3.0
End
Frequencies[1/cm]  15
339.4278               339.9763               666.0166
666.0469               943.1202              1056.2902
1056.6567              1416.3162              1479.4028
1479.6937              2229.8067              3026.9185
3085.7411              3086.1443              3478.9987
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        c10h7
RRHO
Geometry[angstrom]   17
C   -2.342087 -0.789687 0.000182
C   1.23599 1.492987 -0.00007
C   -2.406991 0.622556 -0.000082
C   2.395952 0.795395 -0.00008
C   1.355609 -1.327182 0.000189
C   2.524369 -0.593594 0.000023
C   -1.124987 -1.426414 -0.000392
C   -1.255124 1.371674 0.000158
```

```
C   0.086626 -0.68687 -0.00012
C   0.017308 0.74503 0.000139
H   -3.258566 -1.368743 0.000087
H   1.201705 2.577724 -0.00028
H   -3.373351 1.114428 0.000661
H   1.39504 -2.412201 0.000526
H   3.493202 -1.079675 0.000221
H   -1.073657 -2.510327 -0.000363
H   -1.30436 2.455421 -0.000531
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  45
174.5523              191.9823              368.8691
386.9856              471.7499              485.5864
511.3155              520.6059              611.1652
628.1914              745.0901              754.9555
767.1418              793.9645              805.9451
845.2289              888.1353              936.1904
956.7704              970.6818              996.7989
1040.0912             1049.2482             1141.2669
1161.1784             1172.2344             1208.1577
1250.0871             1276.7535             1334.8589
1385.5649             1394.0363             1457.0524
1468.7884             1530.4230             1592.5026
1620.1890             1656.5683             3155.0771
3158.4833             3159.6258             3164.2142
3175.9226             3179.5633             3188.1262
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  2
End
GroundEnergy[kcal/mol] 0.0
End
!-------c10h7_c3h4_p0a------------
Bimolecular   p0a
Fragment       c3h4
RRHO
Geometry[angstrom]   7
C   -0.7953643067 0.0340930197 0.0003929351
C   1.7999079767 -0.188313622 -0.0384040502
H   -1.2789000818 0.9884787247 0.182918491
H   -1.4365104427 -0.8255826572 -0.1664284561
H   2.3603730273 -0.4130354538 0.8635083944
H   2.3636835038 -0.0613232862 -0.9572540549
C   0.5024913234 -0.0757887252 -0.0189202593
Core  RigidRotor
SymmetryFactor 4.0
End
Frequencies[1/cm]  15
371.2233              371.5183              865.8663
866.2617              884.0403             1016.3687
1016.5866             1109.0953             1422.1712
1479.1925             2051.9260             3118.9601
```

```
3123.0938              3193.6015              3194.4729
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        c10h7
RRHO
Geometry[angstrom]   17
C   -2.342087 -0.789687 0.000182
C   1.23599 1.492987 -0.00007
C   -2.406991 0.622556 -0.000082
C   2.395952 0.795395 -0.00008
C   1.355609 -1.327182 0.000189
C   2.524369 -0.593594 0.000023
C   -1.124987 -1.426414 -0.000392
C   -1.255124 1.371674 0.000158
C   0.086626 -0.68687 -0.00012
C   0.017308 0.74503 0.000139
H   -3.258566 -1.368743 0.000087
H   1.201705 2.577724 -0.00028
H   -3.373351 1.114428 0.000661
H   1.39504 -2.412201 0.000526
H   3.493202 -1.079675 0.000221
H   -1.073657 -2.510327 -0.000363
H   -1.30436 2.455421 -0.000531
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  45
174.5523               191.9823               368.8691
386.9856               471.7499               485.5864
511.3155               520.6059               611.1652
628.1914               745.0901               754.9555
767.1418               793.9645               805.9451
845.2289               888.1353               936.1904
956.7704               970.6818               996.7989
1040.0912              1049.2482              1141.2669
1161.1784              1172.2344              1208.1577
1250.0871              1276.7535              1334.8589
1385.5649              1394.0363              1457.0524
1468.7884              1530.4230              1592.5026
1620.1890              1656.5683              3155.0771
3158.4833              3159.6258              3164.2142
3175.9226              3179.5633              3188.1262
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  2
End
GroundEnergy[kcal/mol] 1.1
End
!-------h_c10h6_p1------------
Bimolecular   p1
Fragment        c10h6
RRHO
```

```
Geometry[angstrom]   23
C   -3.4297275383 0.6926828295 0.0039083678
C   0.2561865651 -1.4034018581 -0.0085023831
C   -3.4192071452 -0.7206557811 -0.0006487593
C   1.4301622887 -0.6884204437 -0.0080385742
C   0.2375332283 1.4304945887 0.0005892895
C   1.4176697405 0.7420283073 -0.0034772169
C   -2.2463676634 1.3923572342 0.0043120379
C   -2.2271153712 -1.4039826096 -0.0046946993
C   -0.9977522925 0.720531113 0.0002165193
C   -0.9860464949 -0.7144502301 -0.0044032352
C   2.8281081359 -1.1220833093 -0.0116269207
C   2.8483269174 1.2348432817 -0.004056437
C   3.6409965108 -0.0519460444 -0.0095010525
H   -4.3754448604 1.222915632 0.0070883174
H   0.2599391198 -2.4888289276 -0.0119952953
H   -4.3573702871 -1.2643043552 -0.0009374379
H   0.217623734 2.5163608324 0.0041197655
H   -2.2529829395 2.477688416 0.0078122976
H   -2.2185160279 -2.4892073171 -0.0081914894
H   3.1434835396 -2.157922306 -0.0153885217
H   3.0748527551 1.8496933954 0.8759822814
H   3.072160391 1.8553276045 -0.8808330576
H   4.7229266941 -0.0789710526 -0.0107867963
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
102.2294             134.8645             251.8437
263.5800             278.6570             394.6986
405.8898             417.1671             426.3605
487.3719             559.6989             578.1974
628.8197             686.4746             732.6775
738.6653             751.4693             764.7804
783.4099             806.1723             857.4753
858.7720             890.3014             902.4118
913.7707             955.6878             957.5792
963.1137             970.5211             991.6628
1043.4534            1077.4282            1121.2771
1155.6730            1169.2853            1174.4788
1180.6497            1244.5385            1251.5039
1268.6960            1282.1901            1347.9739
1373.3697            1387.7710            1434.9787
1446.5223            1470.3410            1486.9167
1537.3526            1611.9868            1627.0456
1655.0763            1677.6805            3013.8854
3035.4208            3153.1920            3155.6051
3159.0651            3162.4123            3173.3962
3186.6618            3189.2638            3212.1926
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        H
```

```
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -36.51
End
!-------h_c10h6_p2------------
Bimolecular   p2
Fragment        c10h6
RRHO
Geometry[angstrom]   23
C   3.3470139691 -0.1784239349 -0.001643978
C   -0.8842205267 -0.4325083205 -0.0072564037
C   2.726429771 -1.4486079448 -0.0077584959
C   -1.6327602416 0.7404671779 -0.0032145561
C   0.3640781219 2.0708040892 0.0046323389
C   -1.0114628758 2.0005023316 0.0027143091
C   2.5833180704 0.9631720545 0.0024139944
C   1.355902182 -1.5520334827 -0.0096475295
C   1.165120296 0.8966729154 0.0005939313
C   0.537531976 -0.3935695503 -0.0055813048
C   -3.0990961767 0.3869034187 -0.0067243045
C   -1.8099242179 -1.5696327613 -0.0128348109
C   -3.0780386636 -1.1207224362 -0.0124526263
H   4.4290830247 -0.1096456294 -0.0001791325
H   3.3379375392 -2.3440222559 -0.0109806364
H   0.860868578 3.0352454583 0.0093447647
H   -1.6062808473 2.908085251 0.0057784256
H   3.0580407341 1.9390508141 0.007080557
H   0.8891185 -2.5303532928 -0.01442073
H   -3.6221352851 0.7853374153 0.8721696031
H   -3.6190854475 0.7919835703 -0.8844308124
H   -1.5129772577 -2.6101143399 -0.0173138716
H   -3.9711972226 -1.7309105476 -0.0167237316
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
113.5257             131.9163             229.2535
241.8649             268.1291             387.6530
432.9010             438.9526             463.5719
506.1584             519.7956             565.0100
613.2436             666.3208             682.0518
723.0441             748.4811             753.1903
798.3278             817.3537             841.0725
879.0965             882.4712             933.2309
950.4010             954.8911             958.7597
966.8124             969.3282             992.8559
1043.9091            1074.2166            1126.1545
1143.1105            1166.9833            1178.4415
1192.0183            1216.8068            1236.5320
1283.2710            1293.5284            1351.7454
1378.3222            1389.1206            1430.1706
```

```
1431.5184              1469.3722              1486.3917
1555.1522              1584.8304              1618.8469
1634.2323              1664.3623              3014.4097
3037.1196              3155.8991              3157.6508
3165.4471              3174.7872              3178.0459
3188.0059              3195.5734              3217.7099
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        H
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -36.19
End
!-------h_c10h6_p3------------
Bimolecular   p3
Fragment        c10h6
RRHO
Geometry[angstrom]   23
C   3.3589805782 -0.1589532841 -0.0052741521
C   -0.8626124942 -0.4592216299 0.0061451685
C   2.7512244302 -1.4362419127 -0.0057558711
C   -1.6304316353 0.7002778521 0.0104255245
C   0.3504445096 2.0582620245 0.0073112859
C   -1.0208972146 1.9753841923 0.0110703316
C   2.58240266 0.9743296087 -0.0010636067
C   1.3828455855 -1.5556845697 -0.0020600345
C   1.1658232353 0.8928735063 0.0028576508
C   0.5497812064 -0.4047593755 0.0022898527
C   -3.0471181043 0.3231433831 0.013518318
C   -1.786615793 -1.65287093 0.0068930735
C   -3.1559300206 -1.0165005908 0.0115352725
H   4.4401442599 -0.0787740034 -0.00823888
H   3.372925776 -2.3247255603 -0.0090822067
H   0.8378607683 3.0277237362 0.0077226495
H   -1.6280620211 2.8741736402 0.0144845493
H   3.0467756867 1.9552584003 -0.0006703734
H   0.9246806356 -2.5385591873 -0.0024656456
H   -3.8673579721 1.0301984874 0.0178637838
H   -1.6405804813 -2.2929696258 -0.8725833972
H   -1.6357579267 -2.2952054346 0.8839587431
H   -4.0761106684 -1.5851637269 0.0138329637
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
111.6057               140.7443               235.7064
237.2840               257.3698               398.3460
432.9203               435.8184               465.2515
517.6631               520.4055               551.8391
```

```
616.8391              670.8841              681.8888
717.6433              751.4780              760.5919
787.6060              828.8756              839.7089
870.5955              872.9566              937.1401
954.7419              955.4339              959.8592
969.6851              982.2343              991.7663
1043.6091             1060.8926             1117.9424
1144.2864             1166.9366             1179.2631
1185.6203             1233.5150             1244.7639
1263.9305             1288.3090             1363.9889
1378.3244             1398.4726             1416.6215
1434.3888             1470.0882             1487.4172
1552.8699             1587.7715             1621.6410
1637.3459             1664.1362             3014.2828
3037.1636             3156.0941             3158.7295
3163.7980             3176.1937             3177.0078
3187.4191             3190.5460             3215.9190
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        H
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -36.33
End
!-------h_c10h6_p4------------
Bimolecular   p4
Fragment        c10h6
RRHO
Geometry[angstrom]   23
C   3.7695852196 -0.0064018801 0.1624634079
C   -0.3681027934 -0.8226648439 -0.1754219653
C   3.3187500647 -1.3444696048 0.0757045779
C   -1.2899850887 0.2105062445 -0.2022003511
C   0.51585409 1.8271389281 -0.004209719
C   -0.8220659745 1.5561515634 -0.1137952259
C   2.8687958828 1.0311253417 0.1375131586
C   1.9775783278 -1.6190602397 -0.0341907195
C   1.4774799929 0.7826568887 0.0249353278
C   1.0200273942 -0.5701457584 -0.0628983946
C   -2.6885215071 -0.0499966899 -0.3160526462
C   -3.8738171039 -0.2543236385 -0.412071668
C   -5.3035998711 -0.5068617608 -0.5273154055
H   4.8310747361 0.1965152437 0.2488677317
H   -0.7141061282 -1.8479727961 -0.2418500721
H   4.0392322254 -2.154399737 0.0964489004
H   0.8579800055 2.8547663717 0.0622144114
H   -1.5472635443 2.3605226794 -0.1350036066
H   3.2126102001 2.0581942628 0.2039493882
H   1.6305100804 -2.6449192567 -0.1008133461
```

```
H   -5.7209994588 -0.8553331929 0.4225559236
H   -5.5092767819 -1.2719180664 -1.2819815849
H   -5.8417039676 0.4008889412 -0.8153441225
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
13.2466                62.5761                74.7243
164.4456               182.3529               269.4018
284.4434               345.5747               373.0123
393.0782               436.4623               485.1788
515.9132               552.1632               557.9209
616.2315               658.6678               661.8111
760.2520               779.5747               781.0217
833.6909               858.7340               874.8436
913.6325               952.6072               964.9148
979.7661               996.7664              1014.7086
1042.2834              1049.7956              1054.1792
1152.0061              1172.8489              1178.1938
1211.5509              1249.9931              1286.9966
1298.8516              1371.5645              1395.9116
1403.2038              1416.5169              1464.4389
1478.0379              1479.1806              1502.0790
1537.4508              1603.0487              1641.3785
1666.7591              2336.3606              3019.6932
3073.9064              3079.7539              3157.6695
3161.4205              3163.8674              3175.3187
3178.1638              3188.2924              3191.9414
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        H
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -9.62
End
!-------h_c10h6_p5------------
Bimolecular   p5
Fragment        c10h6
RRHO
Geometry[angstrom]   23
C                   3.674981    0.497930   -0.000270
C                  -0.219804   -1.159771    0.000398
C                   3.507073   -0.905745   -0.000471
C                  -1.335316   -0.344858    0.000639
C                   0.104371    1.613217    0.000265
C                  -1.150805    1.068039    0.000508
C                   2.577411    1.326248   -0.000042
C                   2.247044   -1.454470   -0.000300
C                   1.265061    0.792212    0.000092
```

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C                  1.093658   -0.627265    0.000071
C                 -2.678275   -0.945911    0.000639
C                 -4.953878    0.338200   -0.001024
C                 -3.818184   -0.297671   -0.000173
H                  4.674304    0.918331   -0.000291
H                 -0.342425   -2.238727    0.000371
H                  4.379634   -1.549380   -0.000766
H                  0.228583    2.691348    0.000169
H                 -2.024495    1.709749    0.000604
H                  2.703431    2.404084    0.000102
H                  2.118144   -2.531928   -0.000473
H                 -2.716374   -2.033955    0.001034
H                 -5.449819    0.614651   -0.927951
H                 -5.451004    0.614896    0.925210
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
46.2339               103.8385              125.7138
182.5167               253.5967              276.1306
328.7230               379.4763              401.6511
411.5401               480.6687              497.2674
525.9436               594.2023              604.9617
644.7759               684.6387              761.7100
766.4329               782.3325              784.1895
836.0403               872.7358              881.4050
888.9360               896.1518              922.2063
963.8350               967.0643              983.3427
995.5075              1012.7378             1042.5921
1102.8136              1151.4380             1174.0129
1179.9562              1197.0911             1240.8038
1280.4937              1289.0527             1327.6220
1393.1879              1397.8004             1412.9141
1461.6268              1483.9705             1506.4370
1544.0494              1609.8810             1643.4084
1667.4288              2033.5041             3102.7160
3118.8576              3154.6031             3157.3764
3159.5801              3162.9618             3171.8426
3174.7675              3182.2671             3187.6613
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        H
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -7.24
End
!-------h_c10h6_p6------------
Bimolecular   p6
Fragment        c10h6
```

```
RRHO
Geometry[angstrom]   23
C                  -3.601815    0.383900    0.302093
C                   0.331336   -1.086775   -0.247675
C                  -3.363878   -1.009966    0.307200
C                   1.382170   -0.220264   -0.431775
C                  -0.134704    1.666895   -0.258174
C                   1.134016    1.177774   -0.433294
C                  -2.561681    1.263041    0.118863
C                  -2.091489   -1.497572    0.129425
C                  -1.236971    0.792021   -0.067861
C                  -0.995906   -0.616759   -0.062344
C                   2.794036   -0.741286   -0.658787
C                   4.583078    0.196625    1.078480
C                   3.776591   -0.228610    0.296433
H                  -4.610267    0.755805    0.444027
H                   0.506299   -2.158545   -0.239833
H                  -4.192432   -1.694002    0.452640
H                  -0.311403    2.737565   -0.261235
H                   1.966220    1.860584   -0.565497
H                  -2.741326    2.333194    0.115215
H                  -1.908480   -2.567183    0.133933
H                   2.788502   -1.834732   -0.616378
H                   3.120378   -0.476294   -1.672758
H                   5.293819    0.569455    1.774398
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  63
21.6630              74.6359              142.6424
180.7269             243.9161              286.6814
331.4442             373.4920              402.0165
408.0951             485.4417              503.1293
526.7069             576.4951              635.5364
658.0474             667.8370              678.5675
737.5344             764.6428              781.4020
786.3882             832.1626              868.5120
878.8089             903.6712              946.9423
958.7772             965.8670              979.7131
985.0094             996.4644             1042.5726
1148.0008            1172.5342             1179.0625
1188.9602            1216.9373             1239.4898
1277.2317            1289.1479             1325.1916
1392.2986            1396.8940             1408.1882
1466.5377            1474.9665             1503.1218
1545.9904            1612.9193             1646.3300
1674.0852            2223.3362             3008.3643
3056.3908            3153.8497             3157.5197
3159.6598            3162.9819             3175.1434
3179.1100            3187.9599             3476.1676
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
```

```
Fragment        H
Atom
Mass[amu]   1
ElectronicLevels[1/cm]        1
0   2
End
GroundEnergy[kcal/mol] -2.25
End
!-------ch3_c12h8_p7------------
Bimolecular   p7
Fragment        c12h8
RRHO
Geometry[angstrom]   20
C                   3.236624    0.172310    0.00
C                  -0.841043   -0.948009    0.00
C                   2.881179   -1.197039    0.00
C                  -1.833267    0.017271    0.00
C                  -0.145939    1.764012    0.00
C                  -1.464948    1.395382    0.00
C                   2.263177    1.142223    0.00
C                   1.559667   -1.569997    0.00
C                   0.889207    0.791807    0.00
C                   0.528778   -0.592960    0.00
C                  -4.379851   -0.646290    0.00
C                  -3.212685   -0.349389    0.00
H                   4.283729    0.453226    0.00
H                  -1.115580   -1.996676    0.00
H                   3.659088   -1.952091    0.00
H                   0.123389    2.814985    0.00
H                  -2.247821    2.143774    0.00
H                   2.535296    2.192583    0.00
H                   1.284563   -2.619418    0.00
H                  -5.408056   -0.912317    0.00
Core  RigidRotor
SymmetryFactor 1.0
End
Frequencies[1/cm]  54
  87.9880              133.1440              181.2468
 218.2255              352.1262              383.4870
 401.5587              429.5214              484.5990
 516.8219              552.4624              559.6133
 629.3281              632.9808              663.6020
 685.9742              691.9308              760.9473
 779.8212              780.6114              834.1419
 876.3712              899.3207              915.5693
 966.6536              971.2117              980.9216
 999.0278             1041.9866             1145.5746
1172.8883             1177.9761             1185.7844
1233.3388             1277.2123             1289.8811
1371.2885             1395.2179             1403.3569
1465.1985             1499.2505             1537.6500
1603.6481             1640.9279             1667.3435
2205.9189             3158.8057             3163.5226
3165.7769             3176.3887             3179.5926
```

```
3189.0981              3194.5312              3477.6126
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
Fragment        ch3
RRHO
Geometry[angstrom]   4
C                   0.000000     0.0000       0.000
H                  -0.9358075   -0.5401365    0.000
H                   0.9358075   -0.5401365    0.000
H                   0.0000       1.080495     0.000
Core  RigidRotor
SymmetryFactor 6.0
End
Frequencies[1/cm]  6
 505.5776              1403.1131              1403.3797
3103.7859              3282.6714              3283.0465
ZeroEnergy[kcal/mol]     0.0
ElectronicLevels[1/cm]        1
0  1
End
GroundEnergy[kcal/mol] -15.3
End

!-------bar_ts0-1------------
Barrier      ts0-1  i1  p0p
RRHO
Geometry[angstrom]   24
C   3.76994   0.01624   0.41853
C  -0.28693  -0.8287   -0.49631
C   3.3644   -1.31764   0.18061
C  -1.14991   0.2194   -0.55546
C   0.52793   1.82404  -0.02216
C  -0.79045   1.55162  -0.31983
C   2.85519   1.03897   0.35397
C   2.05341  -1.60222  -0.11632
C   1.49237   0.78284   0.04936
C   1.08338  -0.56924  -0.19119
H   4.80736   0.22767   0.65208
H  -0.60794  -1.85086  -0.67459
H   4.09504  -2.1172    0.23374
H   0.84704   2.84558   0.16309
H  -1.52524   2.3479   -0.37143
H   3.16487   2.06311   0.5357
H   1.7413   -2.62538  -0.29887
C  -3.41112  -0.22226  -1.06748
C  -4.62584  -0.43934   1.2916
C  -4.0514   -0.33822  -0.04039
H  -3.17228  -0.18452  -2.10395
H  -5.38494   0.33146   1.45299
H  -3.85218  -0.31702   2.05762
H  -5.09881  -1.41373   1.44402
Core  RigidRotor
```

```
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  290.3817
WellDepth[kcal/mol]  44.44
WellDepth[kcal/mol]  2.31
End
      Rotor     Hindered     ! 63 cm^-1   CH3
        Group                 22 23 24
        Axis                  19 20
        Symmetry       3
        Potential[kcal/mol]     4
0     0.103333259 0.223148058 0.123061533
      End
      Rotor     Hindered     ! 10 cm^-1
        Group                 19 20 21 22 23 24
        Axis                  4 18
        Symmetry       1
        Potential[kcal/mol]     8
0.01195343      0.2797124       0.631229467     0.187441507     0
0.321374644     0.77244548      0.210585943
      End
Frequencies[1/cm]  63
                28.7912
                79.0441                 97.7220
176.6484             203.3793              316.3168
348.4021             371.6784              389.1046
477.7321             485.4667              496.9637
515.3030             619.9604              627.8965
657.2454             691.5528              746.3446
768.6028             768.8787              799.7490
813.3370             853.1219              892.6143
931.4543             939.8204              956.9292
969.1551             993.7361             1037.8501
1040.2588            1046.6855             1057.5648
1144.3211            1161.4569             1172.6711
1210.1482            1252.8749             1277.2623
1344.1359            1385.5919             1393.0761
1411.4232            1459.0165             1467.3266
1474.0957            1475.1044             1530.7447
1595.4413            1614.3671             1657.0523
2118.1022            3015.3446             3070.3195
3083.2119            3148.1046             3149.9389
3155.9823            3161.1578             3168.8979
3173.6564            3186.4070             3434.7944
ZeroEnergy[kcal/mol]  2.31
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts1-2------------
Barrier      ts1-2  i1  i2
RRHO
Geometry[angstrom]   24
```

```
C   -3.6991765103 0.5715589621 -0.0082453105
C   0.1412514365 -1.2106173568 0.0327111227
C   -3.5763759946 -0.8357747581 0.0464690616
C   1.2827136024 -0.4344546731 -0.0067634796
C   -0.0942592816 1.5692186668 -0.0754008448
C   1.141906261 0.9817961058 -0.061676544
C   -2.575384954 1.3628969559 -0.0481742656
C   -2.3345984626 -1.4245449156 0.0602129842
C   -1.2807581212 0.7870198245 -0.035349062
C   -1.1546949389 -0.6363933284 0.0199760934
C   2.6168229722 -1.0781892239 0.0083981313
C   3.7826247139 -0.4882426904 -0.0238812471
H   -4.6844319796 1.0239303845 -0.0185614809
H   0.230468771 -2.2923208175 0.0747818701
H   -4.4691669214 -1.4503635938 0.0776323695
H   -0.1838343731 2.6501202707 -0.1174460867
H   2.0367119703 1.5938408085 -0.0927604265
H   -2.6666824861 2.4434966891 -0.0901971912
H   -2.2404081653 -2.5048094314 0.102203717
H   2.5732668394 -2.1752784008 0.0520625286
C   5.0414404221 0.2282552977 -0.0618788086
H   5.1407854075 0.9053855994 0.7958748657
H   5.1270558111 0.8357976334 -0.9716494972
H   5.914361981 -0.4431220088 -0.0422314993
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  229.9263
WellDepth[kcal/mol]  5.28
WellDepth[kcal/mol]  3.21
End
Frequencies[1/cm]  65
32.4267               45.3432
123.3654              129.9946              182.4128
276.3873              298.6003              324.7371
387.8631              403.0819              484.6640
518.9512              524.5410              555.7427
633.5105              639.9821              720.2631
750.9756              780.1446              780.1914
804.5984              835.5812              855.5777
876.7152              914.5850              939.2407
962.3259              974.9320              977.5220
994.1034              996.9307             1025.9402
1042.5261             1142.9842             1171.5683
1175.9770             1188.0821             1234.6328
1272.1696             1281.4879             1289.9437
1387.6760             1394.0300             1405.0048
1410.2414             1450.2695             1469.4698
1471.9188             1498.1351             1542.8688
1608.7994             1640.5962             1665.5352
1808.6714             2945.0512             2974.1684
3003.2755             3037.8531             3151.1478
3155.2547             3156.6042             3161.4629
```

```
3173.7696              3175.1765              3186.8189
ZeroEnergy[kcal/mol]  -36.84
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts2-3------------
Barrier      ts2-3  i2  i3
RRHO
Geometry[angstrom]   24
C   -3.7629695558 0.6187902644 0.0901283413
C   0.0613021541 -1.1672522323 -0.2465481121
C   -3.6387474128 -0.7844949302 0.0842648782
C   1.2475395941 -0.369187977 -0.306068572
C   -0.1637565081 1.6365150515 -0.2621663749
C   1.0661523857 1.0740636388 -0.3582126774
C   -2.631566612 1.4104581951 -0.0176304622
C   -2.3994513246 -1.376313116 -0.0238572519
C   -1.3531654281 0.8393343516 -0.1307505668
C   -1.2178009487 -0.5909423866 -0.1307184082
H   -4.7422058805 1.0755312048 0.1754992386
H   0.1580801056 -2.2477405926 -0.2657275746
H   -4.5267343771 -1.4020330856 0.1651521412
H   -0.2702168308 2.7166411924 -0.2914041657
H   1.9509012625 1.6933909769 -0.4601152407
H   -2.7230668305 2.492224576 -0.0182171189
H   -2.3082859116 -2.4577130919 -0.027692139
C   2.5879104849 -0.985082728 -0.5781508719
C   2.639688458 -0.9098194274 0.7033827115
C   3.162197569 -1.0948416378 2.0598288668
H   3.1218415515 -1.3280317191 -1.458820599
H   2.4790890913 -1.7095863024 2.6537527585
H   3.2664767087 -0.1342502979 2.5730375167
H   4.1433452553 -1.5875149266 2.0473526825
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  495.1615
WellDepth[kcal/mol]  25.79
WellDepth[kcal/mol]  3.5
End
Frequencies[1/cm]  65
62.2443                91.5754
118.2179               161.5623               194.5210
270.8300               277.1322               300.4171
397.2849               407.0803               439.4227
464.1436               506.0859               520.2349
615.7716               626.1579               692.0752
735.6551               738.5551               756.9831
767.0231               800.1802               808.1683
869.9224               875.5091               889.1462
941.2330               943.5352               975.3791
980.5673              1030.5817              1043.5005
```

```
1052.5966             1084.5417             1136.5193
1162.6746             1168.6093             1178.3825
1223.2672             1261.2727             1287.4782
1318.9034             1359.8637             1400.3080
1409.2167             1443.8233             1464.7616
1466.5469             1471.3205             1512.4906
1562.4004             1622.8429             1627.6005
1871.8071             2990.3910             3058.9271
3079.1189             3138.1998             3150.4539
3152.9858             3156.7598             3163.0449
3171.3112             3174.3565             3185.9312
ZeroEnergy[kcal/mol]  -14.26
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts3-4------------
Barrier      ts3-4  i3  i4
RRHO
Geometry[angstrom]   24
C   -3.588856 0.122578 0.121594
C   0.5109 -0.902898 -0.116362
C   -3.205125 -1.230563 0.033565
C   1.522477 0.104935 -0.158968
C   -0.230558 1.802808 0.074402
C   1.084787 1.484662 -0.015039
C   -2.622571 1.113757 0.131701
C   -1.874153 -1.575346 -0.045863
C   -1.255581 0.796286 0.05372
C   -0.857324 -0.580313 -0.041192
C   2.864984 -0.137972 -1.347655
C   2.980895 -0.250293 -0.071725
C   3.901439 -0.570084 1.053345
H   -4.638878 0.384176 0.183566
H   0.808722 -1.944424 -0.177585
H   -3.964958 -2.00443 0.028266
H   -0.532204 2.841617 0.166991
H   1.843119 2.260113 -0.003478
H   -2.914288 2.156993 0.202358
H   -1.582434 -2.618257 -0.115334
H   3.200947 -0.18694 -2.368721
H   3.523613 -1.425401 1.621847
H   3.965558 0.274568 1.74634
H   4.90293 -0.803355 0.6866
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  570.0222
WellDepth[kcal/mol]  3.44
WellDepth[kcal/mol]  23.0
End
Frequencies[1/cm]  65
68.3130               90.9103
```

135.7836	175.1180	189.4649
229.6581	282.2002	360.5092
393.4619	437.0928	470.7090
483.3880	509.2137	525.1297
611.6183	625.9095	646.3562
673.2161	675.6279	742.8164
756.0611	766.8413	806.8120
810.8880	856.2090	871.9601
912.5533	942.3865	946.0790
976.6454	982.3229	1041.4592
1043.5102	1048.4261	1143.1021
1165.7297	1170.0055	1198.5001
1231.4236	1264.7386	1288.2376
1322.7751	1362.4314	1399.0796
1408.7208	1444.5854	1463.7789
1474.9741	1481.4892	1513.9820
1562.4192	1623.3206	1626.8263
1825.8167	3024.1267	3078.2003
3108.8651	3151.9224	3154.3890
3158.1467	3163.5234	3172.4994
3175.6066	3186.7827	3277.6845

```
ZeroEnergy[kcal/mol]  -14.32
ElectronicLevels[1/cm] 1
0  2
End
!----------------------------------
!-------bar_ts4-8------------
Barrier      ts4-8  i4  i8
RRHO
Geometry[angstrom]   24
C   -3.5991862122 0.0838823616 -0.0039122946
C   0.538119891 -0.8206544558 0.0259658928
C   -3.1723207626 -1.2633334935 0.013741405
C   1.4866326755 0.1832019129 0.0187110137
C   -0.2971992837 1.8434256057 -0.0089367875
C   1.0351436248 1.5359567998 0.0008662729
C   -2.6755906493 1.1028045443 -0.0114376403
C   -1.8314229446 -1.5660343577 0.0235304556
C   -1.2869106653 0.8228115271 -0.0016979724
C   -0.8533876674 -0.5379379516 0.0161543919
C   3.8602772288 0.8290852736 0.0214032237
C   2.9516612048 -0.1147731752 0.0290153244
C   3.3778196213 -1.5803221062 0.0490953584
H   -4.6594589387 0.3102848513 -0.0115032775
H   0.8384409503 -1.861364111 0.0394844995
H   -3.9090002751 -2.0588508247 0.0195433399
H   -0.6164677883 2.880639283 -0.0224693057
H   1.7758669965 2.3275304058 -0.0048431655
H   -3.000916506 2.1380108047 -0.0249923855
H   -1.5032851361 -2.60040362 0.0370921427
H   4.5929647932 1.6013873145 0.015165185
H   2.9972475911 -2.1083938116 -0.8307764769
H   2.9888185212 -2.0865931635 0.9380497031
H   4.4640377308 -1.6606256136 0.0552370973
```

```
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  695.1996
WellDepth[kcal/mol]  3.39
WellDepth[kcal/mol]  4.32
End
Frequencies[1/cm]  65
35.6166              88.8854
169.7470             181.8903             228.3699
242.1694             323.1540             351.1277
397.1980             454.1500             462.7956
485.6657             520.7131             527.3926
559.1763             599.6794             631.8000
664.2612             677.1194             759.8259
782.1021             784.0398             833.9823
872.3881             879.8362             906.8406
952.8431             963.4863             978.1540
982.5105             995.5790            1033.5354
1042.9559            1076.0430            1147.9570
1173.7809            1178.6307            1200.6489
1235.0106            1278.8742            1292.3319
1372.8444            1392.9063            1397.2116
1411.1815            1466.7757            1486.0202
1488.8302            1498.7849            1539.8911
1608.4020            1640.8842            1642.7027
1667.4036            3022.4354            3077.3784
3125.4385            3155.5317            3157.3057
3160.9501            3173.9631            3178.6169
3183.7206            3187.4239            3433.6649
ZeroEnergy[kcal/mol]  -33.93
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts8-5------------
Barrier      ts8-5  i8  i5
RRHO
Geometry[angstrom]   24
C   -3.6229139835 0.1254589992 -0.1487551243
C   0.492534337 -0.8708180601 -0.1514305063
C   -3.2260497326 -1.2325584397 -0.147919074
C   1.451112727 0.118177294 -0.1575335261
C   -0.2880730604 1.81363935 -0.156478315
C   1.0429805797 1.478673951 -0.1586966369
C   -2.6784136739 1.1227665965 -0.1504211046
C   -1.8935617418 -1.5658281249 -0.1483257059
C   -1.2935399736 0.812801459 -0.1506887401
C   -0.8917634241 -0.5597901186 -0.1488017975
H   -4.6780050917 0.3750496036 -0.1486756222
H   0.7938141988 -1.9135074658 -0.1594900417
H   -3.9809711277 -2.0108113645 -0.1474588602
H   -0.5874406141 2.8567209169 -0.1642129859
```

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H   1.8013978412 2.253377243 -0.1727249466
H   -2.9806231679 2.1650182298 -0.152171675
H   -1.5883234782 -2.6071290608 -0.149033932
C   3.5981658021 -0.3195703531 -1.2521282798
C   2.9149108669 -0.222765308 -0.1369733865
C   3.5372039084 -0.4305327376 1.2361094387
H   4.6135848062 -0.5348088167 -1.5530933383
H   3.0380186322 -1.2550941071 1.7552476449
H   3.4052238069 0.4660385189 1.8505151336
H   4.6031265631 -0.6539422049 1.1662243815
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  51.6384
WellDepth[kcal/mol]  2.93
WellDepth[kcal/mol]  1.8
End
Frequencies[1/cm]  65
78.2882              146.0952
177.5632              191.7488              197.8492
281.1523              359.1626              367.5052
416.7248              455.3583              486.7135
521.1060              552.4550              566.0342
628.0350              667.3857              676.6094
689.7832              759.6893              780.1439
785.3934              833.4025              847.7952
867.7927              875.5322              913.6508
956.2948              964.4081              977.9071
995.5809              996.9793             1030.1313
1041.4268             1080.7433             1152.6069
1170.6366             1178.3973             1207.4966
1239.8122             1278.2677             1289.4884
1371.8731             1392.8005             1395.2862
1399.7809             1463.8124             1477.8621
1481.0579             1499.5389             1539.2534
1606.2294             1640.5164             1669.2044
1681.0619             3017.2047             3071.9064
3108.4073             3156.2750             3158.9152
3160.7786             3163.5322             3174.5731
3180.9691             3187.4198             3226.3700
ZeroEnergy[kcal/mol]  -35.32
ElectronicLevels[1/cm] 1
0  2
End
!----------------------------------
!-------bar_ts5-6------------
Barrier      ts5-6  i5  i6
RRHO
Geometry[angstrom]   24
C   -3.5868007287 0.1656043728 0.0328652642
C   0.4962542766 -0.8477742354 0.0885484196
C   -3.2180560395 -1.199705721 0.1329780007
C   1.4812807335 0.1100526309 0.0122036154
```

```
C   -0.2284410914 1.7997883558 -0.1054918526
C   1.1114833455 1.4674920496 -0.0872638534
C   -2.6256160055 1.1419242913 -0.0446899109
C   -1.8966791662 -1.5645846663 0.15377219
C   -1.2435331204 0.8132022824 -0.0268967231
C   -0.8728317639 -0.579377391 0.0752319874
H   -4.6368347465 0.4350405238 0.0178748325
H   -3.9909944228 -1.9576770002 0.1933243775
H   -0.5263919417 2.8402826501 -0.1816778522
H   1.8663983841 2.2443435952 -0.1489419957
H   -2.9108135279 2.186400228 -0.1212499223
H   -1.6094241885 -2.6071199718 0.2301857504
H   1.3450155156 -1.9361773992 0.1654995985
C   2.7271350607 -1.842069564 0.151555867
C   2.8335815299 -0.5184033741 0.0523264933
C   4.0997433089 0.2848571204 -0.013886646
H   3.4452440758 -2.6486044844 0.2080917088
H   4.1424660291 0.8666267681 -0.9411254313
H   4.9818237331 -0.355336955 0.0290392019
H   4.1516227501 0.997099894 0.8168198804
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  1985.2121
WellDepth[kcal/mol]  25.29
WellDepth[kcal/mol]  24.62
End
Frequencies[1/cm]  65
83.0835              114.5526
172.0516              179.5260              192.1321
232.2582              297.5574              397.9343
412.8113              453.0482              496.1916
503.6096              521.5282              563.0390
590.0119              647.6322              653.9617
668.4693              681.1581              758.0986
772.6170              794.1662              827.4686
873.1960              883.8911              941.0324
956.3463              968.5779              971.3883
996.0425             1012.6210             1028.2150
1035.7240             1052.2204             1141.3626
1150.4893             1166.2496             1179.4708
1235.2980             1262.1929             1315.1887
1364.0168             1373.0521             1381.0400
1408.6919             1459.2558             1480.5364
1482.5561             1485.5146             1540.0407
1586.8152             1617.4600             1647.4988
1664.4650             1748.3887             3016.1140
3063.2640             3111.2313             3155.2683
3158.4119             3166.4028             3175.3351
3178.4144             3189.1271             3217.9214
ZeroEnergy[kcal/mol]  -11.83
ElectronicLevels[1/cm] 1
0  2
```

```
End
!----------------------------------
!-------bar_ts6-7------------
Barrier      ts6-7  i6  i7
RRHO
Geometry[angstrom]   24
C   -3.8818416507 0.5179733922 0.0923410731
C   0.0741927685 -0.9302104366 0.1943046931
C   -3.6585137401 -0.8453630549 0.3919063271
C   1.151769329 -0.1158667559 -0.0550590859
C   -0.3707225263 1.7239440514 -0.3883020509
C   0.917571213 1.2531200518 -0.3552836936
C   -2.822473284 1.3574020294 -0.1617008093
C   -2.3803696401 -1.3490019296 0.4330485359
C   -1.4891219579 0.8787371969 -0.1294961783
C   -1.266413474 -0.5094202077 0.1757941663
H   -4.8959384498 0.9002799798 0.063662942
H   -4.5038238843 -1.4947681526 0.5899382653
H   -0.5601300746 2.7677725647 -0.6165947774
H   1.7474658767 1.9217874169 -0.5568547851
H   -2.9962719413 2.4038156684 -0.3914889555
H   -2.2036174823 -2.3937801107 0.6622920259
C   3.6537604375 -0.3501508193 -0.1466545171
C   2.4288790482 -0.8501674395 0.0390090904
C   2.1182552688 -2.2868225905 0.386210609
H   3.8112829623 0.6937992234 -0.3949797362
H   4.5391913843 -0.9684291323 -0.0564018362
H   0.7927644011 -2.1048798059 0.421767446
H   2.4250169699 -2.6211281404 1.376749166
H   2.3219994461 -3.0254069989 -0.3883959146
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  1823.649
WellDepth[kcal/mol]  15.79
WellDepth[kcal/mol]  39.94
End
Frequencies[1/cm]  65
47.7513               87.7916
173.7757              192.6830              230.9306
325.2686              348.6520              410.0579
418.5192              452.1716              500.9919
519.5031              521.4468              563.9605
588.0975              639.3369              652.3654
681.8384              728.0673              765.8900
789.1911              797.9509              831.1932
879.0055              894.9549              901.4062
929.8091              961.4452              962.0070
972.8280              997.2662             1033.2269
1040.9221             1041.7961             1132.1362
1147.4397             1170.0022             1179.7117
1234.5315             1238.8738             1263.3445
1306.4911             1362.7349             1365.9334
```

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1397.0405              1426.3130              1448.4897
1462.3296              1486.0932              1537.8860
1590.1835              1628.7694              1652.8016
1669.4116              1725.9372              3077.6711
3135.6816              3152.3194              3156.3528
3159.4385              3167.1740              3177.3461
3178.9267              3189.6819              3216.1468
ZeroEnergy[kcal/mol]  -20.66
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts7-13------------
Barrier      ts7-13  i7  i13
RRHO
Geometry[angstrom]   24
C   3.496209878 -0.1220731838 0.2180543474
C   -0.5732033246 0.819472081 -0.451355826
C   3.1143552293 1.2088839637 -0.0409411006
C   -1.5893702111 -0.1932854716 -0.368837583
C   0.1674718034 -1.8545888379 0.0326831837
C   -1.14041576 -1.5677191837 -0.1634028552
C   2.5369156533 -1.1213979568 0.2482604109
C   1.7920545247 1.5261034674 -0.2599896875
C   1.1806194349 -0.8326065356 0.0295641358
C   0.7821098206 0.5237919145 -0.2264656626
H   4.5390546653 -0.3625249751 0.3892399904
H   -0.8685431355 1.838499976 -0.6767660329
H   3.8681409114 1.9881173278 -0.0675560166
H   0.4769941627 -2.8833864957 0.187842106
H   -1.8860439914 -2.3552210278 -0.1700134991
H   2.8289967749 -2.1489539283 0.4410674462
H   1.5012659596 2.5525149392 -0.4583282594
C   -3.7001633683 0.1627687834 -1.8896956486
C   -2.9762190131 0.0809796308 -0.7877320508
C   -3.0206917399 0.2259665457 0.6503183481
H   -3.2596673201 -0.0194816072 -2.8635047524
H   -4.7547550255 0.4143518004 -1.8493454461
H   -3.3401620241 -0.5953684095 1.2807291615
H   -2.9452599045 1.2054871832 1.1070932908
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  481.4375
WellDepth[kcal/mol]  36.15
WellDepth[kcal/mol]  1.25
End
Frequencies[1/cm]  65
70.6040                81.7781
165.3074               199.3003               216.1263
292.7356               358.3916               384.9391
432.5199               435.8733               471.9568
506.7616               517.7512               609.0075
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623.5365                 668.2990                 680.3744
719.9347                 735.9969                 751.3387
764.7324                 789.0169                 804.2074
836.4330                 869.8436                 887.4860
930.3889                 936.4967                 945.8746
960.9091                 976.0436                 982.2137
1023.0293                1043.8504                1065.8244
1144.2980                1167.6400                1169.9547
1187.4746                1219.6871                1261.6100
1290.3120                1325.5805                1358.7842
1409.8013                1422.7320                1441.9452
1457.9992                1467.0189                1511.3242
1561.3221                1622.1047                1631.6396
1808.6025                3124.1581                3129.3008
3153.4607                3155.6758                3158.9932
3167.0223                3173.2533                3177.2957
3187.4416                3215.9356                3224.7769
ZeroEnergy[kcal/mol]  -24.45
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts13-14------------
Barrier      ts13-14  i13  i14
RRHO
Geometry[angstrom]   24
C   3.4805307629 -0.1527829224 -0.1861075741
C   -0.6315102777 0.8184780489 0.0933407319
C   3.0692772748 1.1949528733 -0.2307313119
C   -1.6107947538 -0.2027369024 0.1792064448
C   0.1689594007 -1.8732369969 0.2109416319
C   -1.152893435 -1.5711252737 0.2853278084
C   2.5383477977 -1.1554857783 -0.0484209388
C   1.7347082737 1.5219682508 -0.1426634622
C   1.1665061997 -0.8560356645 0.0446072353
C   0.7407653961 0.5138233795 -0.0084559145
C   -3.3416272281 -0.0484791572 -2.298364245
C   -2.9982652784 -0.04662194 -1.0387060602
C   -3.0829969278 0.1274810344 0.3836803633
H   4.5335916481 -0.3995628148 -0.2564625067
H   -0.9461301792 1.8567989636 0.0750719871
H   3.8114378901 1.9787740558 -0.335969267
H   0.4927970828 -2.9063217581 0.2877933244
H   -1.890592686 -2.356776972 0.4104940596
H   2.8505152402 -2.1943804762 -0.0078603588
H   1.4225593593 2.5606619345 -0.1789643151
H   -2.6373521891 -0.3004198448 -3.0882558684
H   -4.3568615897 0.2007112584 -2.619098669
H   -3.6465657918 -0.6237365714 0.9395597868
H   -3.2862999894 1.1340782735 0.7547191179
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
```

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ImaginaryFrequency[1/cm]  552.2467
WellDepth[kcal/mol]  9.21
WellDepth[kcal/mol]  20.04
End
Frequencies[1/cm]  65
63.4556               72.2755
154.3139              183.2280               246.7529
265.8908              315.1035               391.7663
401.3315              424.1417               464.1634
500.8942              503.9604               521.3806
613.4106              627.9594               689.1816
739.7619              755.0382               768.6371
802.6995              806.8571               867.4681
872.1982              908.5553               921.7956
943.1635              946.2164               948.2678
970.4691              981.6406              1012.8384
1043.6707             1083.9274              1132.4137
1166.5901             1171.7804              1174.1159
1182.9455             1225.3112              1266.6996
1288.9568             1365.3991              1370.4587
1413.5830             1431.9182              1455.5328
1456.5815             1473.0919              1520.9153
1567.3872             1625.9140              1630.9200
1811.6093             3036.3845              3041.2117
3104.6345             3131.5910              3152.9021
3154.6817             3157.6731              3161.2967
3172.1744             3174.0049              3186.5421
ZeroEnergy[kcal/mol]  -16.49
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts14-15------------
Barrier      ts14-15  i14  i15
RRHO
Geometry[angstrom]   24
C   -3.6381931796 0.5687237009 0.438517266
C   0.1086092049 -1.2963855932 -0.2580781774
C   -3.4897495493 -0.8232137723 0.6383797838
C   1.1758806348 -0.541035156 -0.6785407351
C   -0.1821778085 1.4942891566 -0.6606334797
C   0.9947235226 0.8437696795 -0.8682791983
C   -2.5711305541 1.3248510116 0.0179777706
C   -2.2781904782 -1.430313433 0.413820573
C   -1.3055008572 0.7303245679 -0.2234488197
C   -1.1526135048 -0.6820794744 -0.021262363
H   -4.5992462097 1.0371571451 0.6189135446
H   0.2064613301 -2.3670039374 -0.099916244
H   -4.3384995487 -1.4105221848 0.9704436025
H   -0.2926050192 2.5630899782 -0.8150634318
H   2.2830883593 1.1325774002 -1.2683276063
H   -2.6824793217 2.3931825947 -0.1361212454
H   -2.1649023472 -2.4985935589 0.5673835323
C   2.5957591964 -0.9871643407 -0.9875072348
```

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C   4.5307710461 0.5799157753 -1.783919393
C   3.3099192901 0.2734267616 -1.3991753297
H   3.0719098176 -1.4451841582 -0.1125049994
H   2.6160803878 -1.7345750636 -1.7894390802
H   5.3157620643 -0.1730881796 -1.8673473504
H   4.8128075268 1.5974880821 -2.0361883757
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  1834.8619
WellDepth[kcal/mol]  24.36
WellDepth[kcal/mol]  19.84
End
Frequencies[1/cm]  65
43.4119              113.4332
173.9459              175.4407              258.3364
264.8237              312.4579              373.2318
391.9182              432.6302              480.7253
509.9273              557.7966              562.8356
590.0260              643.6265              648.3027
751.9746              754.8638              776.3413
778.0881              854.5739              871.1259
885.2161              902.1320              909.4661
912.1373              955.0632              956.0757
966.7788              994.4498             1042.4529
1067.0546             1089.7318             1143.1655
1168.7106             1171.6662             1174.9726
1217.6649             1243.0028             1257.6968
1277.2043             1348.2516             1388.2974
1402.1123             1424.6846             1445.3244
1461.9967             1476.0287             1533.8072
1609.1104             1631.9751             1658.1793
1726.1091             1735.4890             3012.2901
3039.3973             3074.8563             3146.4066
3156.3643             3157.6699             3162.2286
3169.0387             3174.4428             3187.1480
ZeroEnergy[kcal/mol]  -12.17
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts14-16------------
Barrier      ts14-16  i14  i16
RRHO
Geometry[angstrom]   24
C   -3.6459303061 0.3230051641 0.1580253701
C   0.3754595695 -0.9238724811 -0.087141799
C   -3.3514322537 -1.05987104 0.1904304491
C   1.401513926 -0.0247031358 -0.1971672571
C   -0.2089165568 1.7683341399 -0.1494275888
C   1.1013245341 1.3585911173 -0.2291765041
C   -2.634125522 1.246392728 0.0481034817
C   -2.051229674 -1.4975717583 0.1125113166
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C   -1.2783993394 0.8368775049 -0.034972831
C   -0.9838222409 -0.5705900573 -0.0016134867
H   -4.6770442965 0.6521617996 0.2205194984
H   1.1355589518 -2.0763165895 -0.0977127075
H   -4.1603596966 -1.7765889647 0.2774726712
H   -0.4485398853 2.826419091 -0.1731780575
H   1.898583925 2.0903439909 -0.3159574306
H   -2.8610115827 2.3075144725 0.0233028168
H   -1.8208692868 -2.5566997036 0.1369804433
C   2.7694145679 -0.6778641634 -0.2716356019
C   3.1927995221 -3.2566515417 -0.2017457813
C   2.4760760041 -2.1529356478 -0.1925955825
H   3.2891449887 -0.4225630412 -1.2033698168
H   3.4174687349 -0.3540068633 0.5521164173
H   4.2806245565 -3.2366277474 -0.2819046249
H   2.7346453601 -4.2383002731 -0.1299433947
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  1836.7489
WellDepth[kcal/mol]  23.83
WellDepth[kcal/mol]  18.79
End
Frequencies[1/cm]  65
51.7861              111.7265
157.2918              169.1925              250.8709
262.2797              313.8908              387.6156
412.2045              471.5348              495.4771
509.5303              514.9701              554.1863
563.4579              641.5179              651.7169
736.5858              753.1768              778.7085
797.7136              820.7294              877.0657
895.1438              910.7621              936.1128
950.7713              962.5021              972.3043
973.2643              996.2412             1040.5871
1040.7551             1095.4464             1140.9118
1164.1746             1167.6574             1172.8969
1202.8400             1234.6950             1259.1305
1292.4016             1365.0604             1371.5734
1390.0518             1424.4849             1458.5661
1463.3997             1489.9967             1538.1530
1589.6900             1633.7118             1661.5994
1726.4216             1740.0278             3006.4598
3031.8991             3075.0358             3152.3173
3156.4389             3166.1261             3168.6207
3171.7061             3178.1978             3188.9897
ZeroEnergy[kcal/mol]  -12.7
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts15-17------------
Barrier      ts15-17  i15  i17
```

```
RRHO
Geometry[angstrom]   24
C   -0.1009863622 -0.6413943597 0.0669605441
C   -1.5129241897 -1.2262975441 0.1267092102
C   -2.4155360612 -0.1221574557 -0.3574847198
C   -2.2634148373 1.106196934 0.2133992338
C   -0.0087189753 0.7610705448 0.0066957474
C   1.1526743152 1.4603441893 -0.05428818
C   2.3808112705 0.7291264758 -0.0653410143
C   2.3327539715 -0.7020911808 -0.0041662042
C   1.0729504015 -1.3597941914 0.0624784523
H   -1.597819414 -2.130975847 -0.4792668577
H   -1.7474871924 -1.5108562502 1.1611680519
H   -2.8890653677 -0.2191664988 -1.3289162558
H   -1.9712464 1.2105556944 1.2527646311
H   -2.6893116855 1.9938916416 -0.2421935133
H   1.1796229439 2.5450874774 -0.0982697091
H   1.0550571205 -2.445973121 0.1059018237
C   4.8071527991 0.6405354966 -0.1445388556
C   4.7625885319 -0.7711624461 -0.0837349118
C   3.643276487 1.371444268 -0.1363225644
C   3.5552173234 -1.4235760108 -0.0160450132
H   5.7654486779 1.1451482157 -0.1978387542
H   5.6870300693 -1.3376775139 -0.0910316061
H   3.6753796694 2.4551251874 -0.1832530562
H   3.5208389041 -2.5073267054 0.0297765213
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  417.0066
WellDepth[kcal/mol]  10.83
WellDepth[kcal/mol]  44.17
End
Frequencies[1/cm]  65
69.9086              114.4662
191.6696              233.6131              254.5551
297.7749              393.8645              397.4929
421.2474              479.6463              489.8505
524.6141              555.5788              623.1846
635.0302              681.5692              723.2970
753.9803              771.6017              775.2417
848.9654              853.7004              867.7043
894.4591              903.4378              921.3709
940.6993              954.7401              960.4611
964.4494              992.7961             1042.3821
1081.0420             1138.4413             1167.7780
1169.5527             1203.9975             1215.6754
1237.2066             1266.1656             1274.8515
1289.2590             1344.2389             1387.4071
1398.8457             1421.1839             1439.0030
1472.6548             1480.2958             1531.5712
1564.2559             1604.6850             1622.7128
1655.8238             2999.2021             3078.7614
```

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3126.1363             3139.5968             3149.9249
3155.8352             3160.9781             3161.3104
3173.5632             3186.4111             3207.2985
ZeroEnergy[kcal/mol]  -21.18
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts16-18------------
Barrier      ts16-18  i16  i18
RRHO
Geometry[angstrom]   24
C   -0.1432039942 -0.5803318662 0.0369707311
C   -1.5258759072 -1.2307635757 0.0427413195
C   -2.4726788448 -0.1294462158 -0.3552930455
C   -2.342219832 1.0723776643 0.2771326436
C   -0.0912721248 0.7834708035 0.0173503292
C   1.0867804783 1.5468484064 0.0240267514
C   2.3245309056 0.8117621713 0.0401411363
C   2.2806716151 -0.6088887133 0.056613786
C   1.0865904957 -1.290353917 0.0572334104
H   -1.5710322967 -2.0802564178 -0.6437429668
H   -1.7477003216 -1.6223971428 1.0450277988
H   -2.9679621436 -0.1875103007 -1.3189181701
H   -2.0380610529 1.1320414566 1.3162709889
H   -2.8073067917 1.9668516734 -0.1241473645
H   3.2178408947 -1.1556065919 0.0690265699
H   1.0804011567 -2.3764876717 0.0724394522
C   2.3283340649 3.631668952 0.0140752384
C   3.5466079174 2.9127852157 0.0280086362
C   1.1268429987 2.9656000087 0.0112082135
C   3.5429412978 1.5387163977 0.0397604594
H   2.347459705 4.7157533709 0.004274987
H   4.4866416842 3.4530724896 0.0290494597
H   0.1898455737 3.5104110502 -0.0032974899
H   4.4786345217 0.9885627527 0.0505591255
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  424.2524
WellDepth[kcal/mol]  10.17
WellDepth[kcal/mol]  44.68
End
Frequencies[1/cm]  65
81.8095              111.2943
185.4572              206.1254              243.1694
290.5527              408.2988              414.5569
448.0430              493.3601              501.4352
516.3327              531.8734              606.8830
637.5621              654.9188              739.3103
753.0058              765.1792              776.1009
817.2667              874.8398              876.1157
911.7520              925.5851              943.5622
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956.1049              958.5528              967.1779
969.3345              995.0029             1039.4755
1083.8976             1136.0867             1166.2766
1170.2372             1199.0524             1202.9898
1234.3784             1259.6136             1275.0374
1294.2257             1360.9109             1364.6547
1388.2157             1421.9694             1453.4587
1479.4952             1490.1698             1528.0272
1564.6986             1583.7174             1635.9549
1661.1497             2994.0570             3067.2195
3126.7929             3146.4089             3155.1423
3161.4757             3165.5927             3170.3377
3178.7808             3188.9098             3207.0571
ZeroEnergy[kcal/mol]  -21.32
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts2-9------------
Barrier      ts2-9  i2  i9
RRHO
Geometry[angstrom]   24
C   -3.670911 0.563115 -0.055287
C   0.172469 -1.207409 0.028436
C   -3.542428 -0.844515 -0.090372
C   1.32134 -0.429923 0.077482
C   -0.071491 1.570716 0.103473
C   1.167602 0.990582 0.124772
C   -2.550161 1.358218 0.006523
C   -2.299602 -1.430047 -0.062941
C   -1.255085 0.786221 0.035457
C   -1.12213 -0.637798 -0.000211
C   2.630173 -1.079581 0.099849
C   4.514936 0.664363 -0.282089
C   3.832494 -0.479426 0.200913
H   -4.657241 1.012598 -0.077245
H   0.263411 -2.289273 0.005079
H   -4.43239 -1.462099 -0.138919
H   -0.165013 2.65142 0.141785
H   2.047898 1.617492 0.190634
H   -2.645441 2.438968 0.034107
H   -2.201707 -2.510448 -0.089445
H   2.602942 -2.16698 0.122732
H   5.355744 1.05674 0.281791
H   4.136162 1.280112 -1.1017
H   4.932392 -0.57563 -0.484838
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  1840.5094
WellDepth[kcal/mol]  42.2
WellDepth[kcal/mol]  67.84
End
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Frequencies[1/cm]  65
44.8884              111.0161
123.5777              182.7056              224.6447
246.0666              356.9728              386.0985
394.5739              419.0170              436.2324
485.3116              525.4288              548.8213
614.9455              643.7327              661.0778
756.9064              762.4833              780.7614
781.6549              829.8254              837.5241
872.5340              877.8592              893.1396
908.0433              960.9959              963.1615
977.7526              992.8993             1033.0360
1041.6315             1047.5297             1130.4938
1147.9022             1174.0803             1181.2397
1197.2480             1242.6988             1285.0576
1289.5353             1327.3065             1391.8523
1398.0698             1411.1548             1457.9116
1470.9604             1498.4362             1539.7948
1592.2819             1602.0953             1637.3727
1663.0839             2179.2987             3034.8536
3120.0971             3153.4469             3156.1211
3158.6145             3161.8742             3171.5300
3173.9154             3186.9488             3193.0413
ZeroEnergy[kcal/mol]  2.15
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts2-12------------
Barrier      ts2-12  i2  i12
RRHO
Geometry[angstrom]   24
C   -3.7727890263 0.2863751064 -0.2136799032
C   0.3336324293 -0.7156336317 0.0321040207
C   -3.3335043518 -0.9973423667 -0.6094816565
C   1.2626176909 0.2124099837 0.4961132915
C   -0.5247868595 1.8319269816 0.8202901151
C   0.799667178 1.5048519581 0.9021841118
C   -2.867068717 1.2121330215 0.2529721114
C   -2.0029240536 -1.332697886 -0.5317519429
C   -1.4902022405 0.8999692345 0.3444887581
C   -1.0421561725 -0.4004880431 -0.0547093461
C   2.6433183229 -0.1334831167 0.650630221
C   3.8723105991 -0.3911901764 0.353809568
C   4.9019770383 -0.3701022832 -0.7246392218
H   -4.8250348671 0.5385701437 -0.27969995
H   0.6685998008 -1.7013982441 -0.2710215211
H   -4.053973872 -1.7200153239 -0.9763335487
H   -0.858124332 2.820345851 1.1198967706
H   1.5212559947 2.2248087565 1.2706196442
H   -3.2002604955 2.1992094138 0.5572894806
H   -1.6673931483 -2.3188809422 -0.8355715168
H   3.4271098279 -0.4468974138 1.598360145
H   4.4527746578 -0.057731903 -1.6769636705
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H   5.3497737299 -1.358364457 -0.8540998213
H   5.7064378665 0.3263253369 -0.4753191393
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  2063.8455
WellDepth[kcal/mol]  45.52
WellDepth[kcal/mol]  51.41
End
Frequencies[1/cm]  65
38.3242              56.5027
106.5917             143.9561              179.3810
210.7578             234.0482              277.6966
359.0963             381.0999              396.6021
436.9417             478.7727              515.3278
541.5490             551.0481              621.7835
650.9750             659.2419              754.2864
775.9563             776.6025              824.8125
848.5920             861.7357              892.1744
933.2267             956.2777              974.3634
975.2726             989.6517             1026.3258
1029.9818            1042.2281             1139.2416
1170.5084            1175.2967             1181.7476
1229.0756            1273.5844             1287.6262
1356.9008            1383.8837             1388.1801
1403.5557            1460.6388             1465.8389
1475.4320            1487.9764             1530.7444
1588.1034            1629.3027             1653.1133
1967.3961            2298.2520             2987.1793
3073.4829            3094.9856             3155.6344
3158.7775            3161.2537             3171.9116
3174.4061            3183.1341             3187.2601
ZeroEnergy[kcal/mol]  5.47
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts9-10------------
Barrier      ts9-10  i9  i10
RRHO
Geometry[angstrom]   24
C   0.0643016429 -0.4228854266 -0.1237875015
C   1.3897298712 -0.8910148288 -0.2028115431
C   2.582806753 -0.0456520088 -0.4043629242
C   3.3507965018 0.444956116 0.5667686131
C   -0.2534541888 0.9831233054 -0.1767453424
C   -1.5412375719 1.420319688 -0.1021463528
C   -2.6347284779 0.5108781109 0.0348348289
C   -2.3489414783 -0.8926718316 0.0936355221
C   -1.0104680552 -1.3254259313 0.0121772803
H   1.5448951689 -1.9671888212 -0.1738278164
H   2.8588381221 0.1674953458 -1.4400551945
H   3.1290161417 0.2642375623 1.6134684153
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H   4.2278332655 1.0429326546 0.3436366448
H   0.5593168297 1.6930348805 -0.2715068389
H   -1.7567356226 2.4833585 -0.1447654678
H   -0.8011555407 -2.3899006145 0.0553860384
C   -3.9752839429 0.9432762239 0.1148327007
C   -5.0061510846 0.0360926901 0.2478909686
C   -4.7298087586 -1.3474923105 0.3063337141
C   -3.4339968816 -1.8013990241 0.23118785
H   -4.1859588077 2.0069435583 0.0697634652
H   -6.0315449284 0.3825866228 0.3080214394
H   -5.5464570533 -2.0530680102 0.4109277826
H   -3.2218749043 -2.8646144509 0.2759017181
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  176.0874
WellDepth[kcal/mol]  10.16
WellDepth[kcal/mol]  6.47
End
Frequencies[1/cm]  65
58.9884              118.1762
143.3594              186.5372              265.7495
284.2813              380.4698              392.5955
449.1184              474.9843              493.4555
516.1377              522.6251              617.3919
630.5494              660.8328              696.4010
756.6212              772.2065              772.8247
795.0997              827.3279              857.3025
885.7284              886.2816              951.1393
957.6710              959.9595              985.7775
989.4040              991.4129             1014.6431
1042.4218             1097.0442             1145.4287
1165.3729             1172.6588             1202.2104
1235.9989             1275.2230             1290.7650
1315.1615             1339.4717             1380.6597
1403.6935             1420.7562             1452.0834
1471.4569             1482.3140             1529.4492
1573.0427             1622.1227             1640.3165
1685.8856             3066.8506             3127.4896
3131.0439             3155.6143             3157.5864
3158.6182             3162.7295             3174.8984
3188.0176             3188.9740             3212.8347
ZeroEnergy[kcal/mol]  -55.53
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts10-11------------
Barrier      ts10-11  i10  i11
RRHO
Geometry[angstrom]   24
C   -3.3739532523 -0.704195826 0.2102618768
C   0.3321079162 1.3453331891 -0.1274975412
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C   -3.3244095633 0.6919479127 0.3921330466
C   1.4797690611 0.6620262567 -0.4065720699
C   0.2077095433 -1.4411678799 -0.5677662002
C   1.4417111064 -0.7754455026 -0.6686786223
C   -2.2266103601 -1.4074286318 -0.0859313278
C   -2.1221946551 1.3630651738 0.2714399208
C   -0.9752521461 -0.7497610903 -0.2101411625
C   -0.9307625381 0.6745010228 -0.0319171198
C   2.8471559923 1.1543615733 -0.2297821526
C   3.0331010124 -1.0420290375 0.7008520554
C   3.6638662686 0.2283695206 0.3088550897
H   -4.3199098866 -1.2257236294 0.3051636068
H   0.3737292178 2.4053531832 0.1043445728
H   -4.2312230356 1.2384837711 0.6247705428
H   0.1403130886 -2.4928423342 -0.8258961787
H   2.1584629406 -1.1621295561 -1.3868609753
H   -2.2655680998 -2.4826500851 -0.2273757269
H   -2.0830576113 2.4388723645 0.4097172439
H   3.1452496515 2.1689305874 -0.4672785354
H   3.5757319853 -1.9712426586 0.5439125781
H   2.4233495128 -1.0356124382 1.60002074
H   4.7296158513 0.3954821143 0.444608339
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  621.5095
WellDepth[kcal/mol]  29.46
WellDepth[kcal/mol]  23.64
End
Frequencies[1/cm]  65
87.0073              120.4135
193.8175              237.5361              286.0566
373.3478              390.9271              415.7222
457.4084              477.5963              526.8128
550.8634              597.2274              625.7282
645.7777              697.3885              731.8933
746.7738              758.7195              767.0185
793.4221              815.4478              818.7634
867.6585              890.9094              907.7001
942.8676              946.9894              952.1300
978.6937              983.1936             1018.6405
1045.8767             1071.5331             1131.4842
1146.3334             1160.5607             1173.5546
1182.2031             1223.0369             1264.8283
1286.9847             1340.4356             1367.7386
1377.3147             1409.3005             1447.9204
1463.4458             1481.7870             1515.1094
1571.4150             1601.4991             1628.7793
1633.2321             3098.7111             3127.7735
3134.1847             3153.4812             3155.7699
3159.5911             3164.9142             3173.2998
3179.1937             3186.5178             3187.2287
ZeroEnergy[kcal/mol]  -32.54
```

```
ElectronicLevels[1/cm] 1
0  2
End
!---------------------------------
!-------bar_ts11-p1------------
Barrier      ts11-p1  i11  p1
RRHO
Geometry[angstrom]   24
C   -3.4161438987 -0.7006126056 0.0442542038
C   0.2505748051 1.4366481775 0.0112789432
C   -3.4182470513 0.7118164046 0.002333923
C   1.4318570431 0.7422279309 0.0134792004
C   0.2518916741 -1.4022025397 0.0602640149
C   1.4405948539 -0.7013218814 -0.0420101523
C   -2.2266650169 -1.3890986047 0.0625873534
C   -2.2315107672 1.407009672 -0.0173981907
C   -0.9831193735 -0.7052893886 0.0385278868
C   -0.9855906829 0.7313394804 0.0002815872
C   2.8189811523 1.1890458287 0.0952635723
C   2.8717797653 -1.1704433589 0.1746376969
C   3.6419402452 0.1291895689 0.1758934097
H   -4.3569356707 -1.2391150222 0.0603955891
H   0.2388938465 2.5216348836 0.036533428
H   -4.3611342106 1.2468451352 -0.012689904
H   0.2465869783 -2.4867971317 0.1031272278
H   1.5799159402 -0.7667877778 -1.908343318
H   -2.2225555069 -2.4738791022 0.0918442281
H   -2.2342754444 2.4917755546 -0.0462141572
H   3.1224621046 2.2282584996 0.0988003843
H   3.2233463442 -1.8717554671 -0.5870037976
H   2.9650742172 -1.6799011958 1.1431078996
H   4.720848653 0.1725469397 0.2497909715
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  781.0149
WellDepth[kcal/mol]  25.88
WellDepth[kcal/mol]  6.21
End
Frequencies[1/cm]  65
102.2842             131.8339
249.2988             262.0147             280.6743
382.1412             390.5720             413.0913
424.7886             470.9704             482.5557
528.8816             558.2109             578.6936
627.6745             694.4021             732.3464
745.8256             748.1660             765.1017
779.6125             805.6296             853.4539
856.6266             884.5213             902.9943
913.6281             954.6612             957.2314
963.2458             971.9009             991.9228
1043.3690            1074.9416            1122.2664
1160.3921            1167.4599            1172.5039
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1179.3466            1241.3644            1249.0100
1270.9740            1282.9909            1348.9356
1372.5964            1383.9238            1427.8524
1444.8274            1459.0676            1484.4678
1531.9691            1601.2034            1617.7054
1649.5553            1653.7774            3010.0272
3065.3924            3156.6358            3160.1185
3161.4879            3164.2620            3175.0274
3188.0466            3190.5188            3212.6235
ZeroEnergy[kcal/mol]  -30.3
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts17-p1------------
Barrier      ts17-p1  i17  p1
RRHO
Geometry[angstrom]   24
C   -3.4369578331 0.699696125 -0.0486182351
C   0.2402614229 -1.4032714515 0.11476639
C   -3.431640392 -0.7118613356 0.0271930958
C   1.4145539726 -0.6917912282 0.0959723728
C   0.2316509305 1.4259228209 -0.0349559104
C   1.4093791552 0.7342530315 0.0219705851
C   -2.2518320656 1.3955101098 -0.0694397383
C   -2.2423500575 -1.3975733853 0.080737623
C   -1.0054560598 0.7209352702 -0.0162292488
C   -0.9992869648 -0.7119312129 0.0614334405
C   2.8159995184 -1.1352648554 0.140940076
C   2.8400136329 1.2280571847 0.033322442
C   3.6314907978 -0.0481038022 0.1639045731
H   -4.3808073277 1.2315641793 -0.0906769188
H   0.2411595473 -2.4873322443 0.1651261945
H   -4.3716991825 -1.2519015628 0.0425885025
H   0.2164642023 2.5103606366 -0.0899849907
H   -2.2548793033 2.4792355334 -0.1276599684
H   -2.2373209736 -2.4812230356 0.1383096626
H   3.1242375647 -2.154704391 0.3305457
H   3.0377996964 -1.7191708869 -1.7517158024
H   3.0381401978 1.9179435674 0.8631555812
H   3.0967958085 1.7714954761 -0.8861628943
H   4.7109197126 -0.0740495431 0.2313574681
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  622.3339
WellDepth[kcal/mol]  33.17
WellDepth[kcal/mol]  4.33
End
Frequencies[1/cm]  65
101.0191             130.6583
238.5014             260.5263             267.6723
284.0391             339.3300             400.4518
```

```
407.3612              419.4070              464.9340
487.9126              565.1893              578.5002
628.8708              703.1001              730.0184
732.6100              750.6896              761.8662
782.9217              804.6804              856.1237
859.4452              888.6001              904.6448
913.7844              953.8285              957.7055
965.4928              978.3205              992.9148
1043.3144             1073.1750             1114.9212
1152.3385             1169.4191             1173.8758
1179.5237             1244.0658             1250.0400
1267.9018             1282.4122             1346.3839
1371.7265             1388.7757             1431.1763
1443.3502             1471.5625             1485.1794
1533.1696             1555.5160             1620.3513
1654.1445             1678.4667             3004.3221
3028.6417             3154.5124             3156.7573
3160.4458             3164.8346             3174.1907
3187.2735             3197.5379             3216.2095
ZeroEnergy[kcal/mol]  -32.18
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts18-p2------------
Barrier      ts18-p2  i18  p2
RRHO
Geometry[angstrom]   24
C   3.3467707902 -0.1785645617 0.0283128244
C   -0.8816778736 -0.4308823346 0.0772987843
C   2.7266341807 -1.4474179326 0.0880953707
C   -1.6321784739 0.736130503 0.0179818621
C   0.3623896443 2.0670396569 -0.0625745804
C   -1.0124464836 1.9960327066 -0.0543042517
C   2.583000004 0.962201947 -0.0181305528
C   1.356140247 -1.5512903354 0.1040311628
C   1.1651668353 0.895098189 -0.005705428
C   0.5386850548 -0.3934255842 0.0615287619
C   -3.1000284955 0.3871655742 0.0465062112
C   -1.8059199662 -1.5749763316 0.1380467099
C   -3.084326966 -1.1118664159 0.1685428543
H   4.4287631125 -0.1100948359 0.0169816551
H   3.3385110245 -2.3419746037 0.1195807407
H   0.8580145605 3.0307197271 -0.1141791825
H   -1.60855089 2.9014505345 -0.0999804279
H   3.0574186703 1.9369425639 -0.0676418429
H   0.8891385175 -2.5285052108 0.1443867391
H   -3.6267749799 0.8603741702 0.8852338262
H   -3.6182466881 0.7157557167 -0.8650690172
H   -1.676550226 -2.21782164 -1.7679862611
H   -1.511687486 -2.5982159243 0.3245781513
H   -3.9761071127 -1.7189895784 0.2426998906
Core  RigidRotor
SymmetryFactor  0.5
```

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End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  584.6788
WellDepth[kcal/mol]  33.76
WellDepth[kcal/mol]  3.95
End
Frequencies[1/cm]  65
112.4164             129.4980
220.0739             236.9861             257.0120
277.0483             325.2868             411.4650
432.8203             459.6675             465.0089
506.9468             520.0546             573.4841
612.4456             680.1152             681.7616
715.6635             749.0727             752.7342
795.8643             818.3622             838.5234
878.6929             881.4388             931.3389
955.4615             958.3760             964.0995
968.9134             970.9573             994.0877
1044.3388            1071.3674            1118.2353
1141.5589            1167.5365            1178.7593
1190.5671            1216.4532            1236.6844
1283.2221            1295.0235            1351.1644
1378.1271            1391.3406            1426.5056
1430.1058            1469.1431            1486.5262
1534.1385            1559.4398            1606.6074
1630.8603            1665.1349            3005.3037
3029.5644            3156.7955            3158.7443
3166.7688            3175.6821            3179.5194
3189.3967            3204.2806            3222.7236
ZeroEnergy[kcal/mol]  -32.24
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts18-p3------------
Barrier      ts18-p3  i18  p3
RRHO
Geometry[angstrom]   24
C   3.349603819 -0.1594102526 0.0679420742
C   -0.8707816038 -0.4482471378 -0.0565759073
C   2.7378703675 -1.4343031043 0.0898152056
C   -1.6309329152 0.7114966643 -0.1145524203
C   0.3505332656 2.0645921519 -0.0952555357
C   -1.0201847235 1.9847794732 -0.1326320294
C   2.5777738292 0.9755630688 0.0073462511
C   1.3695355147 -1.550060269 0.050393885
C   1.1617005376 0.8976080754 -0.0339763704
C   0.5420048961 -0.3974444147 -0.0121681545
C   -3.0553133895 0.3404122391 -0.1384823921
C   -1.793557454 -1.643687926 -0.0524545841
C   -3.158287826 -1.0144518751 -0.1519753011
H   4.4305061182 -0.0821729935 0.0994283084
H   3.3560972073 -2.323824692 0.1382419823
H   0.8405272018 3.0325394855 -0.1097156133
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H   -1.6254114514 2.8836673056 -0.172484604
H   3.0453978028 1.9547221748 -0.0091659716
H   0.9082011463 -2.5312612362 0.0680849631
H   -3.5279554691 0.7342791839 1.777385027
H   -3.8647175197 1.0371023739 -0.3106965168
H   -1.6010891699 -2.3276028261 -0.8890391808
H   -1.6917225942 -2.2430939383 0.8628032418
H   -4.0776085899 -1.5820215306 -0.1978263569
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  589.455
WellDepth[kcal/mol]  33.74
WellDepth[kcal/mol]  4.06
End
Frequencies[1/cm]  65
109.5879             136.2343
229.1242             235.9090             245.0631
272.7382             327.4880             415.3083
433.3986             456.8034             466.0924
520.4280             520.7401             559.3633
616.6651             680.9692             682.6230
714.6209             751.3308             759.5856
787.1069             827.9317             837.1055
870.3633             873.6078             934.1078
956.0166             958.5071             969.0396
972.1533             981.2748             993.1017
1044.0631            1059.1819            1110.1577
1143.6812            1167.3835            1179.3712
1185.0134            1232.9051            1241.4102
1266.3958            1288.5925            1361.1555
1377.9802            1397.9462            1415.9582
1432.6389            1467.9509            1488.4644
1535.2150            1561.8297            1611.9057
1630.6281            1663.3817            3004.8694
3029.4418            3157.2792            3160.8015
3164.7244            3177.0407            3179.4833
3188.0262            3199.0570            3219.6524
ZeroEnergy[kcal/mol]  -32.27
ElectronicLevels[1/cm] 1
0  2
End
!----------------------------------
!-------bar_ts12-p4------------
Barrier      ts12-p4  i12  p4
RRHO
Geometry[angstrom]   24
C   3.8494578241 0.0133955988 -0.0961380097
C   -0.2911225313 -0.8265479342 0.0948842842
C   3.4021715112 -1.3283169831 -0.0691067797
C   -1.2174944552 0.204481585 0.1310021555
C   0.5859118177 1.8319946724 0.0403996317
C   -0.7531367127 1.5549402461 0.102302238
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C   2.9443252415 1.0471454419 -0.0607866765
C   2.059655448 -1.6108033656 -0.0071516199
C   1.5517938601 0.7908698527 0.0032861888
C   1.0977969537 -0.5660036235 0.0310897513
C   -2.6119376481 -0.0645497721 0.1980216906
C   -3.8064177326 -0.2793046881 0.1818474905
C   -5.2210016373 -0.5379921904 0.4408899057
H   4.9120872249 0.2224954824 -0.1453491184
H   -0.635976408 -1.8540768318 0.1148228041
H   4.1263542287 -2.1345973167 -0.097955158
H   0.926694903 2.8618680895 0.0177568432
H   -1.4820615265 2.3556052228 0.1287871922
H   3.2860561589 2.0767512387 -0.0819579015
H   1.7147407221 -2.6392681578 0.0131765332
H   -3.9955378372 -0.3148420439 -1.924446239
H   -5.4091081128 -0.5775786362 1.5181810984
H   -5.5337759884 -1.4895547788 0.003768454
H   -5.8492683039 0.2471568919 0.0127612413
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  425.5057
WellDepth[kcal/mol]  39.64
WellDepth[kcal/mol]  3.32
End
Frequencies[1/cm]  65
53.4538              62.5422
74.9951             136.8194             165.3837
183.0263             279.2070             305.6283
328.0119             373.6550             391.5432
402.1043             466.4501             485.3588
515.7630             557.2344             558.8004
617.5982             659.0138             661.7259
760.7467             779.0749             781.0812
833.6406             858.2031             875.6439
914.2711             951.5970             966.1441
981.2822             998.0836            1011.2170
1042.2855            1045.2865            1061.1751
1151.9282            1173.3863            1178.4243
1211.2272            1249.5762            1287.5086
1298.8388            1371.2273            1395.5124
1403.9579            1414.9346            1464.3868
1476.3920            1480.5800            1500.7272
1536.6110            1601.4894            1639.2873
1664.2171            2277.5550            3026.1221
3085.0693            3092.5693            3158.8822
3162.8109            3165.2170            3176.4407
3180.0431            3189.1717            3193.7348
ZeroEnergy[kcal/mol]  -6.3
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
```

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!-------bar_ts10-p5------------
Barrier      ts10-p5  i10  p5
RRHO
Geometry[angstrom]   24
C   3.7176063655 0.4397991611 -0.2198045521
C   -0.1810126658 -1.1477607017 0.206516409
C   3.539714603 -0.9513492883 -0.0423743251
C   -1.2892244623 -0.3201350659 0.178268639
C   0.1626547981 1.601637467 -0.1432067191
C   -1.094376738 1.080552585 -0.0035420782
C   2.6285222929 1.2789324974 -0.2538351213
C   2.2779855606 -1.4775418628 0.0976633787
C   1.3148682553 0.7685076619 -0.112225737
C   1.133255225 -0.6386370002 0.0673025448
C   -2.6255804039 -0.8950244064 0.3427409195
C   -4.8613534202 0.4490275384 0.5319987218
C   -3.7707293302 -0.231896156 0.3133457752
H   4.7182309799 0.8424189608 -0.3292011187
H   -0.3127829333 -2.2171552134 0.3406848292
H   4.4058317397 -1.603049824 -0.0175392785
H   0.2957855625 2.6695796129 -0.2824282136
H   -1.9615121089 1.7300243229 -0.0326005969
H   2.7629443913 2.3469994616 -0.3902593249
H   2.140791899 -2.5453262961 0.2333449753
H   -2.6757052484 -1.9771450066 0.4486507682
H   -5.5489430404 0.7185291699 -0.2615885092
H   -5.11455657 0.7655256172 1.5412174422
H   -4.0835297514 -0.6113502345 -1.7575938286
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  500.7306
WellDepth[kcal/mol]  58.13
WellDepth[kcal/mol]  3.37
End
Frequencies[1/cm]  65
47.6557              85.2762
110.5325             137.5091             183.2667
254.4873             284.0922             373.2322
383.3305             404.4625             413.4310
427.1121             483.5446             503.6452
525.5981             599.3716             609.1604
644.5790             685.7759             761.2275
767.5694             782.0567             784.0150
835.9268             871.8041             888.9631
891.7821             895.8046             919.4966
964.8807             966.7452             985.1021
996.7166            1009.3820            1042.6344
1094.6169            1150.5578            1174.4815
1179.9030            1197.2920            1241.5470
1281.7074            1289.4384            1327.8247
1393.1864            1398.3897            1413.5533
1458.3294            1481.7288            1503.4538
```

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1543.4078              1607.9909              1641.1639
1664.3641              1982.7975              3110.0526
3123.2332              3156.1935              3158.5898
3161.0835              3164.1597              3175.6998
3185.1014              3188.4279              3192.0679
ZeroEnergy[kcal/mol]  -3.87
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts14-p5------------
Barrier      ts14-p5  i14  p5
RRHO
Geometry[angstrom]   24
C   -3.7006996718 0.459886483 0.0768176268
C   0.2225030897 -1.121154173 -0.068785298
C   -3.5068556878 -0.939719976 0.0256416308
C   1.3187265175 -0.283849154 -0.0648231172
C   -0.1534246469 1.6437441538 0.0305525446
C   1.111888968 1.1224979334 -0.0162025219
C   -2.6195967402 1.3090930962 0.0792347463
C   -2.2374050245 -1.463651412 -0.0218478524
C   -1.2974988004 0.8008471187 0.0310678402
C   -1.1002134688 -0.614362694 -0.0202641297
C   2.6818347582 -0.861209845 -0.1087571485
C   4.9143658784 0.4717882255 0.2385615272
C   3.8002221262 -0.1876530465 0.133598917
H   -4.7074667793 0.860399578 0.1138955162
H   0.3655001602 -2.1965403764 -0.1140279636
H   -4.3671409224 -1.5996052412 0.0236682876
H   -0.2972818636 2.7186957887 0.0674532692
H   1.9731792802 1.7805748493 -0.0160351039
H   -2.765748666 2.3836386144 0.117907282
H   -2.0883700685 -2.5377086581 -0.0619484471
H   2.740514863 -1.9469482194 -0.0824859129
H   2.8253553792 -1.0988441689 -2.0142144548
H   5.454303015 0.80883063 -0.645162875
H   5.3541113045 0.7105224936 1.203796637
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  717.5388
WellDepth[kcal/mol]  34.68
WellDepth[kcal/mol]  5.39
End
Frequencies[1/cm]  65
42.7687              100.0024
116.5452              182.0797              222.2443
251.0710              268.1260              369.5522
383.0397              407.9560              410.2979
464.0060              485.2776              507.5019
526.1080              586.5718              608.2310
644.3548              678.5813              761.0165
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765.4852              782.4542              784.4510
835.2266              873.7566              883.8304
886.9472              907.2581              955.2278
964.8236              967.1568              982.8166
995.6373              996.4339             1042.3969
1086.0679             1150.4375             1173.8510
1180.7377             1192.5428             1238.9812
1278.6955             1288.9328             1320.3166
1393.2198             1397.1820             1410.4812
1452.3378             1479.5000             1504.2094
1545.2929             1610.7479             1643.6301
1668.5182             1979.6187             3087.7720
3127.5976             3155.8410             3157.8430
3158.1680             3160.7331             3163.7437
3175.3896             3183.6475             3188.1502
ZeroEnergy[kcal/mol]  -1.85
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts14-p6------------
Barrier      ts14-p6  i14  p6
RRHO
Geometry[angstrom]   24
C                  -3.665301    0.426868    0.288838
C                   0.245669   -1.108675   -0.239035
C                  -3.450897   -0.970833    0.292792
C                   1.311310   -0.258726   -0.414552
C                  -0.173803    1.652802   -0.245336
C                   1.087790    1.143283   -0.414048
C                  -2.609477    1.288831    0.114358
C                  -2.185887   -1.479576    0.122096
C                  -1.291623    0.795913   -0.064367
C                  -1.074540   -0.616801   -0.060727
C                   2.715577   -0.803206   -0.634902
C                   4.561672    0.147183    1.036704
C                   3.699283   -0.314026    0.326861
H                  -4.668321    0.815341    0.424559
H                   0.402674   -2.183234   -0.233529
H                  -4.291779   -1.641024    0.431569
H                  -0.332500    2.726229   -0.247084
H                   1.931839    1.812489   -0.540645
H                  -2.771190    2.361802    0.111328
H                  -2.021051   -2.552120    0.125470
H                   2.693149   -1.896820   -0.602991
H                   3.059086   -0.533390   -1.643168
H                   5.221754    0.454269    1.811200
H                   5.757696    1.218238   -0.288805
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  450.6795
WellDepth[kcal/mol]  37.63
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WellDepth[kcal/mol]  3.35
End
Frequencies[1/cm]  65
23.0358               43.3061
77.1121              143.5213              180.8725
215.6388              250.6938              290.0201
366.9439              402.0135              407.3253
411.0428              485.9321              503.9890
526.6255              577.6872              635.5863
658.3751              667.8629              737.4287
752.2448              765.0766              781.3207
786.5692              832.8690              868.9186
878.5749              903.0521              941.7408
958.8030              966.0046              980.7192
985.1612              997.3401             1042.6079
1148.1454             1172.7595             1179.1794
1188.7823             1213.4614             1238.5026
1277.1847             1289.1681             1322.2129
1392.5186             1397.1355             1408.2386
1461.3924             1474.6256             1503.1973
1546.1495             1613.0883             1646.3885
1674.1010             2170.9902             2997.7885
3055.9136             3153.9269             3158.0270
3160.4406             3163.5144             3175.5814
3179.6240             3188.3237             3463.2031
ZeroEnergy[kcal/mol]  1.1
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts2-p4------------
Barrier      ts2-p4  i2  p4
RRHO
Geometry[angstrom]   24
C   -3.9020997809 0.2518136142 -0.0488626414
C   0.1947809317 -0.7950470074 0.0744444134
C   -3.5232082297 -1.1075865264 0.0453710048
C   1.1731976037 0.1803459961 0.0238456178
C   -0.5453529917 1.8972738776 -0.1117533893
C   0.7781465902 1.5505298235 -0.0711355949
C   -2.9447922606 1.2367210887 -0.1006697586
C   -2.1951889477 -1.4561389203 0.085965346
C   -1.5658762768 0.9107770484 -0.0607558918
C   -1.181086136 -0.4633006839 0.0344739606
C   2.5770100181 -0.1178816178 0.0672593491
C   3.7894124901 -0.0124709791 0.1046758511
C   5.2385880491 -0.1021591758 0.1486882169
H   -4.9537245897 0.5136497042 -0.0801175676
H   0.4874348821 -1.8362983541 0.145223437
H   -4.2879648048 -1.8749937328 0.0853931494
H   -0.8298544407 2.9418534365 -0.1842607142
H   1.5484002863 2.3109411586 -0.1105104358
H   -3.2341859092 2.2800262842 -0.1730215343
H   -1.9023487045 -2.4982522787 0.1580729554
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H   2.6136624354 -2.1234064065 0.0321745949
H   5.6404529314 0.3788701268 1.0455004212
H   5.6939306305 0.3762658804 -0.7235357686
H   5.5531362236 -1.1516853564 0.159890979
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  558.1328
WellDepth[kcal/mol]  35.51
WellDepth[kcal/mol]  5.08
End
Frequencies[1/cm]  65
19.9912               68.5063
93.1169               97.0580              170.4822
182.4707              266.4483              284.8931
337.4801              395.9449              397.9627
444.5423              484.9825              518.7388
525.6564              554.8158              581.7702
617.0338              660.2545              668.3550
761.0202              780.3007              781.6594
832.6040              855.5958              876.7714
921.7636              953.3995              966.0228
979.4538              997.9412             1017.4385
1041.9349             1043.1509             1052.1448
1152.2320             1173.3088             1179.0925
1209.1156             1243.5111             1282.7710
1291.4211             1374.4422             1394.5864
1406.2107             1412.8189             1464.0474
1470.6395             1476.0896             1501.0236
1535.3366             1604.8772             1641.7016
1667.2802             2248.1687             3013.6115
3069.5251             3077.6418             3157.8036
3162.4745             3164.2868             3173.7743
3176.1097             3188.3850             3192.9934
ZeroEnergy[kcal/mol]  -4.54
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts2-p5------------
Barrier      ts2-p5  i2  p5
RRHO
Geometry[angstrom]   24
C                  -3.758652    0.450192    0.000004
C                   0.165116   -1.136492   -0.000003
C                  -3.565308   -0.950229    0.000004
C                   1.264976   -0.300905   -0.000004
C                  -0.209363    1.630692   -0.000003
C                   1.055457    1.108402   -0.000004
C                  -2.676547    1.298557    0.000001
C                  -2.295604   -1.476035    0.000001
C                  -1.354738    0.788413   -0.000001
C                  -1.157696   -0.627760   -0.000001
```

```
C                    2.618742   -0.877437   -0.000004
C                    3.748950   -0.216297    0.000001
C                    4.913022    0.385477    0.000008
H                   -4.765473    0.852246    0.000005
H                    0.307448   -2.212952   -0.000003
H                   -4.426056   -1.609520    0.000005
H                   -0.353262    2.706317   -0.000003
H                    1.917258    1.766154   -0.000006
H                   -2.822195    2.373871    0.000001
H                   -2.147055   -2.550920    0.000001
H                    2.676951   -1.965726   -0.000008
H                    5.385854    0.700969    0.925771
H                    5.385861    0.700978   -0.925750
H                    6.350538   -1.220885    0.000006
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  364.4727
WellDepth[kcal/mol]  35.69
WellDepth[kcal/mol]  2.88
End
Frequencies[1/cm]  65
45.8409              93.7806
118.9777             168.8815             183.6629
218.6258             266.4369             289.1780
360.9017             387.4330             402.5178
421.3181             484.0472             509.5588
526.0192             605.1940             612.8658
644.4237             694.4512             762.6646
763.7477             782.1298             784.1393
835.4413             873.3269             887.3219
896.5254             897.0431             921.9579
964.3822             966.7676             982.5125
996.4094            1017.2344            1042.6303
1091.0918            1150.7966            1174.1896
1180.0138            1196.0201            1240.3339
1279.8506            1289.0112            1323.7799
1393.0392            1397.3946            1412.7416
1460.2518            1481.2507            1505.3257
1543.8836            1609.8265            1643.4395
1667.6830            2000.1882            3105.2836
3109.1033            3155.8287            3158.2324
3160.1051            3163.5986            3175.4678
3180.3865            3181.3439            3188.2396
ZeroEnergy[kcal/mol]  -4.36
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_tsa-7------------
Barrier      tsa-7  i7  p0a
RRHO
Geometry[angstrom]   24
```

```
C   -4.0000109749 0.4033492002 -0.4659012376
C   -0.0367350294 -0.9925940733 0.1238179299
C   -3.6903460802 -0.9571717598 -0.6964008755
C   0.8911719755 -0.0883163644 0.5317801026
C   -0.6612899427 1.7137689997 0.5862191771
C   0.6257167597 1.261695255 0.7844921381
C   -3.0223550294 1.2747416149 -0.0514365825
C   -2.4102269012 -1.419602457 -0.508506621
C   -1.6888891965 0.8328453842 0.1533865017
C   -1.3772557879 -0.5457537556 -0.0812950446
H   -5.0140129902 0.7555027833 -0.6182281862
H   0.2115953324 -2.0350302603 -0.0511365777
H   -4.4702205032 -1.6359856912 -1.0233140694
H   -0.9066725754 2.7568413428 0.762753119
H   1.4073192655 1.9320798944 1.1241670705
H   -3.258589672 2.3189395608 0.1258756438
H   -2.171836953 -2.4633413023 -0.6849040882
C   3.3185568028 -0.3849476197 2.1125522344
C   3.3065430915 -1.5202479849 -0.2243054859
C   3.1016973696 -0.8782222627 0.9009846148
H   4.0387601981 0.4132090402 2.264454946
H   2.7151229539 -0.6825948091 2.9630029756
H   2.7153919709 -1.3514933305 -1.1143074048
H   4.093290916 -2.2681324047 -0.27542328
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  370.7338
WellDepth[kcal/mol]  64.34
WellDepth[kcal/mol]  2.61
End
      Rotor     Hindered     ! 25 cm^-1
        Group                 18 19 21 22 23 24
        Axis                  4 20
        Symmetry       2
        Potential[kcal/mol]     4
0     0.082433425 0.062369433 0.880468746
      End
Frequencies[1/cm]  64
               43.2367
75.5997              94.8366              165.6363
181.3044             230.5669              242.4409
372.3333             389.3906              393.6208
477.5358             490.1562              514.3201
515.5837             619.8558              629.9287
746.8745             763.7663              765.9630
775.6131             807.8901              813.1685
827.6224             853.3466              884.7754
891.9249             930.4192              957.8761
969.6901             994.7007             1006.6454
1020.7432            1038.0773             1045.6731
1072.4831            1144.0000             1161.2406
1172.4382            1210.3374             1252.0985
```

```
1277.2443              1343.8608              1385.6497
1393.7395              1427.1614              1459.1857
1464.5729              1475.4377              1531.6100
1595.7472              1614.8263              1656.9876
1927.9493              3119.6821              3123.7609
3151.0548              3153.4389              3156.9892
3162.4044              3174.2672              3174.7098
3186.7835              3201.1444              3218.0625
ZeroEnergy[kcal/mol]  3.74
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_tsa-14------------
Barrier      tsa-14  i14  p0a
RRHO
Geometry[angstrom]   24
C   -1.9710088797 -0.9466165477 0.4306779248
C   1.1959351256 1.7891338222 -0.2715424956
C   -2.2356031472 0.4420268274 0.3890991995
C   2.4410617339 1.2765203027 -0.4517012704
C   1.7154587641 -0.9759124684 -0.1856843299
C   2.745620596 -0.0886533986 -0.4127137875
C   -0.6923308972 -1.4126912569 0.2446953618
C   -1.2177673516 1.3366883096 0.1623214106
C   0.3842337481 -0.5180749075 0.0080776596
C   0.1139396663 0.8883010499 -0.0339010793
H   -2.7831645927 -1.6419879703 0.610260077
H   0.9958493558 2.8566314802 -0.3038299099
H   -3.2488627225 0.7986900812 0.5373145868
H   1.9112644605 -2.0435985584 -0.1512697909
H   3.7616263477 -0.4404131491 -0.5571939067
H   -0.4872408557 -2.4778484983 0.2763707923
H   -1.4204890636 2.4022353139 0.1302347381
C   4.2429634293 2.7581772852 -0.8840468176
C   6.2022085117 2.0387064747 0.7004465884
C   5.2650428174 2.4366880665 -0.1086874157
H   4.2109021539 2.4288297687 -1.9168011999
H   3.5927066754 3.5834087266 -0.6143456439
H   6.0461667943 1.203596124 1.3802700633
H   7.1737653302 2.5248161223 0.7350642451
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  239.2847
WellDepth[kcal/mol]  39.53
WellDepth[kcal/mol]  1.87
End
      Rotor     Hindered     ! 12 cm^-1
        Group                19 20 21 22 23 24
        Axis                  4 18
        Symmetry       1
        Potential[kcal/mol]     8
```

```
0     0.130493757 0.291590529 0.001067394 0.031020309 0.031012151 0.0346812
      0.046290127
      End
Frequencies[1/cm]  64
                33.8973
67.1787              113.9326              177.2693
200.3338              321.2507              343.7576
367.5468              378.6628              388.6248
476.7878              487.5111              496.7706
515.4107              620.1171              628.9492
745.7566              751.1684              766.8062
771.3702              814.1119              847.2915
859.3780              870.2684              872.8879
889.8419              936.8604              957.9717
969.7716              994.6538              999.1959
1031.9700             1038.6551             1047.2935
1069.9930             1145.3106             1161.8744
1173.1998             1211.6244             1254.0434
1277.5746             1345.8875             1386.1275
1393.5996             1420.4004             1460.4570
1465.8396             1469.4568             1531.7856
1596.0864             1615.2271             1657.2332
1974.8042             3094.2402             3124.3435
3141.2065             3149.9294             3156.6926
3161.7556             3162.5280             3169.8006
3174.3456             3187.1507             3200.9196
ZeroEnergy[kcal/mol]  3.0
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts10-19------------
Barrier      ts10-19  i10  i19
RRHO
Geometry[angstrom]   24
C   3.5415655422 0.5283386696 0.2733729652
C   -0.2259627703 -1.3430225814 -0.2112450856
C   3.4561468646 -0.8829936358 0.2219898673
C   -1.3781369885 -0.5919289578 -0.3187504277
C   -0.0620915103 1.4451886333 -0.1081694856
C   -1.2775810347 0.8270625198 -0.2635909044
C   2.4067809566 1.2949609284 0.1664333304
C   2.2386563227 -1.4990984632 0.0643704881
C   1.1336080441 0.6898524102 0.0033112709
C   1.0464922809 -0.7364524395 -0.0492698765
H   4.5087560592 1.0022063251 0.3979478556
H   -0.2856665859 -2.4259598523 -0.2493873093
H   4.3589768496 -1.477233825 0.307848525
H   -0.0032375459 2.5280922446 -0.0669001322
H   -2.1828332748 1.4181952395 -0.3448480862
H   2.4695952522 2.3775908133 0.2058998034
H   2.1721212128 -2.5814538623 0.0249340176
C   -2.7023644831 -1.2365984092 -0.5102657461
C   -3.312386698 -1.4278392428 1.8749855409
```

```
C   -3.5570950851 -1.5960873129 0.5257641781
H   -3.0199044303 -1.4243458817 -1.5324897277
H   -4.0387751364 -1.7370653649 2.6155820568
H   -2.3901904109 -0.9843338105 2.230277194
H   -4.5026204307 -2.0513101447 0.2391216883
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  69.8626
WellDepth[kcal/mol]  2.9
WellDepth[kcal/mol]  3.1
End
Frequencies[1/cm]  65
67.8243              157.5799
173.8269              175.4641              298.4633
326.1858              398.5906              403.4319
444.2652              485.4007              505.6832
521.8203              525.4738              598.6160
634.6266              667.9718              697.4769
738.1726              769.5193              780.6064
789.7737              809.6093              835.5701
872.8868              900.1543              919.7046
963.4460              970.8201              977.8654
994.6662              995.5600             1027.9459
1041.3933             1112.2176             1153.1265
1170.4738             1177.8639             1194.9317
1221.7119             1243.1394             1275.9898
1288.7286             1364.4843             1390.7664
1398.2672             1425.2334             1447.9288
1461.6116             1501.8120             1520.7968
1536.8603             1603.8413             1640.6813
1668.9666             3126.5557             3143.3211
3150.0833             3156.5052             3158.7634
3161.5035             3164.5559             3174.6728
3180.8674             3187.2827             3240.7940
ZeroEnergy[kcal/mol]  -59.1
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts19-20------------
Barrier      ts19-20  i19  i20
RRHO
Geometry[angstrom]   24
C   3.647561846 0.4742217112 -0.0683128381
C   -0.1900111136 -1.2428831077 0.5713021381
C   3.5402275859 -0.8338738872 0.4468775145
C   -1.3460372568 -0.4600387513 0.2832909219
C   0.0388804033 1.416453359 -0.3736958093
C   -1.2111349783 0.8585592113 -0.1719907623
C   2.5151136907 1.2052175852 -0.3500542077
C   2.2961116209 -1.3897685978 0.6600836017
C   1.2230286832 0.6614184698 -0.1410424807
```

```
C   1.1175237974 -0.6739143666 0.3601843735
C   -2.5724928599 -1.2530473695 0.2090619345
C   -1.0021588934 -2.8679854125 -0.6539121014
C   -2.3731052131 -2.5050053367 -0.2473524862
H   4.6276836859 0.9066101794 -0.2365727672
H   -0.2701715624 -2.0070908108 1.3365869438
H   4.4364440226 -1.3991801317 0.6756597957
H   0.1309331789 2.4361770607 -0.7308996052
H   -2.1027800908 1.4297632635 -0.4093134374
H   2.59921526 2.2159468708 -0.7359448562
H   2.2097756921 -2.3980617937 1.0524741486
H   -3.5514684428 -0.8453521087 0.4357719172
H   -0.6090836016 -3.8421234182 -0.3743216485
H   -0.656995998 -2.5091501384 -1.6205425886
H   -3.1876304563 -3.2219034798 -0.3258647006
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  638.8802
WellDepth[kcal/mol]  29.22
WellDepth[kcal/mol]  31.74
End
Frequencies[1/cm]  65
99.4242              107.1809
167.1875              221.8877              266.6939
356.0410              410.7650              429.5283
455.5837              487.7448              518.9563
541.0534              556.3296              613.4703
653.6072              674.5092              711.8163
731.6470              750.3336              774.4498
786.7626              802.8058              828.5291
877.8900              889.1340              942.1589
955.2309              956.4267              962.3481
975.4885              989.7994             1009.0763
1046.2136             1061.0969             1132.1317
1154.9764             1158.3829             1175.3983
1196.1748             1227.4254             1261.9997
1283.5966             1334.7080             1365.5998
1373.5134             1390.1160             1450.4765
1453.0605             1487.8586             1534.7365
1561.4917             1589.8197             1610.4898
1645.8394             3095.9836             3126.8734
3145.0017             3155.8541             3158.1965
3160.7622             3173.8081             3177.1672
3177.8425             3179.3364             3187.4929
ZeroEnergy[kcal/mol]  -32.98
ElectronicLevels[1/cm] 1
0  2
End
!----------------------------------
!-------bar_ts20-p3------------
Barrier      ts20-p3  i20  p3
RRHO
```

```
Geometry[angstrom]   24
C   3.6199469131 0.4847184479 0.0398827217
C   -0.2668666042 -1.2105180837 0.0730829471
C   3.4727822653 -0.9169862608 0.1301720974
C   -1.3752133056 -0.3744111308 -0.1384633342
C   0.0458975145 1.5594576995 -0.1726072525
C   -1.2189194353 1.0236567708 -0.2306178432
C   2.5091003313 1.2903794219 -0.0478438886
C   2.2203001493 -1.4868341109 0.1373585158
C   1.2034872791 0.7377878694 -0.0523311489
C   1.0580473972 -0.6840765418 0.0474282532
C   -2.5705671344 -1.2053947201 -0.2458517453
C   -0.7319891516 -2.6494565398 -0.0260095753
C   -2.226414709 -2.5042539886 -0.1737677195
H   4.6117977494 0.9222579997 0.0396901635
H   -0.4449688671 -1.140227121 2.0482195302
H   4.353994101 -1.545183066 0.197556559
H   0.1843971033 2.6332552076 -0.2438399718
H   -2.0839624148 1.6650645803 -0.3586987705
H   2.6189805435 2.3676102889 -0.1193916885
H   2.1149463933 -2.5629224648 0.2179732322
H   -3.5739525608 -0.8175536304 -0.3678706685
H   -0.4531628582 -3.2639330328 0.8353147178
H   -0.2994482909 -3.133923589 -0.91213115
H   -2.9022024086 -3.3477480054 -0.2201399811
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  629.0042
WellDepth[kcal/mol]  32.58
WellDepth[kcal/mol]  4.19
End
Frequencies[1/cm]  65
114.2836             133.5814
233.9749             238.8545             255.4998
376.7410             399.8687             425.0452
432.8509             444.1231             480.3414
521.0521             529.5830             553.3525
618.1347             673.7523             684.4805
720.3311             751.2028             761.9177
792.1620             830.7460             839.3761
868.7640             876.4799             933.3138
955.7548             958.0825             960.3169
971.3406             984.5602             992.7733
1046.1015            1059.9232            1118.6689
1149.6490            1165.8012            1178.8203
1183.7411            1233.7718            1246.1699
1267.3775            1289.7339            1357.1926
1372.8745            1394.7314            1407.6994
1436.2232            1464.2200            1481.3264
1551.6801            1575.3398            1609.3041
1627.9994            1657.6823            3011.3370
3062.2763            3157.7390            3160.7227
```

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3165.7743            3177.8975            3178.8533
3188.7192            3193.0592            3216.6704
ZeroEnergy[kcal/mol]  -32.14
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts9-p5------------
Barrier      ts9-p5  i9  p5
RRHO
Geometry[angstrom]   24
C   3.7230963898 0.3981884795 0.1045934107
C   -0.216180129 -1.1175823297 -0.1884371107
C   3.5151860596 -0.9733334296 -0.1676603909
C   -1.3088632159 -0.2865729714 -0.0170807913
C   0.18677235 1.5929910821 0.3501019211
C   -1.083631181 1.0948264111 0.2548604106
C   2.6500150916 1.2413097881 0.2750336787
C   2.2399992557 -1.4763172288 -0.2643822681
C   1.3231311327 0.7544945998 0.181955641
C   1.1111540402 -0.6327620513 -0.0934616396
C   -2.6606909348 -0.8410031893 -0.109626281
C   -4.8845183661 0.4499800769 0.3688468306
C   -3.7925025814 -0.1648290416 0.0076824997
H   4.7340862502 0.7826144415 0.1783233404
H   -0.3709009592 -2.171364307 -0.399563067
H   4.3689319656 -1.6282897929 -0.3004737177
H   0.343134266 2.6469077092 0.5560571035
H   -1.9381712902 1.7489997033 0.3829223818
H   2.8074994988 2.2944400198 0.4837518173
H   2.0797967047 -2.5288606624 -0.4738640978
H   -2.7324035411 -1.9007820247 -0.3471977539
H   -5.5193148677 0.9731901762 -0.3371813665
H   -5.1933610988 0.4474609274 1.4116388906
H   -3.9857548395 0.1236356139 -2.0923104416
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  500.7546
WellDepth[kcal/mol]  61.82
WellDepth[kcal/mol]  3.37
End
Frequencies[1/cm]  65
47.6575              85.2753
110.5319             137.5114             183.2656
254.4871             284.0916             373.2378
383.3285             404.4638             413.4317
427.1200             483.5448             503.6453
525.5979             599.3704             609.1608
644.5793             685.7748             761.2283
767.5703             782.0584             784.0121
835.9263             871.8056             888.9636
891.7817             895.8024             919.4968
```

```
964.8809              966.7458              985.1017
996.7165             1009.3821             1042.6348
1094.6155             1150.5576             1174.4822
1179.9034             1197.2921             1241.5485
1281.7073             1289.4390             1327.8259
1393.1880             1398.3901             1413.5540
1458.3241             1481.7277             1503.4535
1543.4082             1607.9912             1641.1641
1664.3633             1982.7973             3110.0547
3123.2356             3156.1934             3158.5940
3161.0843             3164.1602             3175.6998
3185.1052             3188.4277             3192.0692
ZeroEnergy[kcal/mol]  -3.87
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
!-------bar_ts0-8------------
Barrier      ts0-8  i8  p0p
RRHO
Geometry[angstrom]   24
C   3.8633115301 -0.0440794168 0.4589066793
C   -0.1956131419 -0.7757107773 -0.5388711269
C   3.4331506641 -1.3620297341 0.1795217729
C   -1.0414716307 0.2880749698 -0.5628159708
C   0.668462941 1.8448319925 0.0146385202
C   -0.6504672173 1.6087075605 -0.3092268926
C   2.9716528658 0.9996604004 0.408381422
C   2.1210308113 -1.6102190511 -0.1440281117
C   1.608394198 0.7810114319 0.0780979564
C   1.1742369898 -0.5549596173 -0.2040016007
H   4.9013193597 0.1385398753 0.7131708494
H   -0.5321951423 -1.7831201044 -0.7661123371
H   4.1457055042 -2.1783558897 0.2218830273
H   1.007673679 2.8552741353 0.223363542
H   -1.3620721668 2.4258458162 -0.365116992
H   3.3006028557 2.0116177142 0.6217135451
H   1.7903092524 -2.6211873369 -0.358771022
C   -3.2751057825 -0.066080178 -2.3254303348
C   -3.785972882 -0.1910688378 0.2627838996
C   -3.2600711642 -0.0820984077 -1.1056494094
H   -3.0630822686 -0.0142089083 -3.3662440418
H   -4.8656251739 -0.3611160585 0.2330390177
H   -3.5921150827 0.7205690926 0.8324180175
H   -3.3154969982 -1.0178686707 0.7991515905
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  364.7857
WellDepth[kcal/mol]  41.71
WellDepth[kcal/mol]  3.46
End
      Rotor     Hindered     ! 158 cm^-1   CH3
```

```
        Group                   22 23 24
        Axis                    19 20
        Symmetry       3
        Potential[kcal/mol]      4
0     0.67872755  1.281321244 0.644327475
      End
      Rotor     Hindered     ! 22 cm^-1
        Group                   18 19 21 22 23 24
        Axis                    4 20
        Symmetry       1
        Potential[kcal/mol]      8
0     0.004344876 1.044571916 0.368266553 0.041007124 0.520076811 0.745740554
      0.385257003
      End
Frequencies[1/cm]  63
                44.1099
66.9173               152.6870
179.4465              224.6088              245.0673
360.6165              382.9342              390.1903
478.8857              491.0492              509.9220
515.8088              571.6787              623.9236
631.3283              679.4860              747.2507
766.8444              768.2011              781.7072
812.9915              854.3476              892.4799
917.9061              935.0115              957.4057
969.2578              994.7451             1029.4248
1041.5414             1053.8436             1065.4472
1144.9833             1162.1065             1172.9189
1210.9202             1253.9223             1277.7853
1346.1862             1385.5650             1393.6082
1414.4197             1459.3954             1467.7252
1477.0597             1481.2383             1531.2536
1596.1948             1614.1237             1657.1665
2070.3004             3033.7439             3097.6832
3100.8197             3146.7032             3147.9644
3155.6171             3160.5144             3167.2053
3173.3798             3186.3646             3454.9822
ZeroEnergy[kcal/mol]  3.46
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------

!-------bar_ts8-p7------------
Barrier      ts8-p7  i8  p7
RRHO
Geometry[angstrom]   24
C                  -3.607398    0.177020    0.152335
C                   0.460048   -0.951104   -0.151188
C                  -3.247648   -1.189527    0.213804
C                   1.441269    0.007563   -0.310815
C                  -0.244628    1.753846   -0.273876
C                   1.070530    1.381312   -0.366920
C                  -2.641319    1.141496   -0.005446
```

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C                  -1.929975   -1.565153    0.116598
C                  -1.272109    0.787733   -0.108779
C                  -0.907222   -0.593792   -0.046290
C                   3.778198   -0.850127   -1.064184
C                   2.833363   -0.377225   -0.435119
C                   3.540936    0.188144    1.635808
H                  -4.651026    0.460175    0.230020
H                    0.737239   -1.998382   -0.109269
H                   -4.019142   -1.941098    0.337834
H                   -0.516729    2.802833   -0.327641
H                    1.845292    2.127387   -0.496294
H                  -2.915632    2.190252   -0.053746
H                  -1.652781   -2.613097    0.162854
H                   4.746340   -1.198606   -1.337691
H                   2.885754   -0.458225    2.206385
H                    3.306610    1.245493    1.639920
H                    4.589797   -0.077848    1.612070
Core  RigidRotor
SymmetryFactor  0.5
End
Tunneling      Eckart
ImaginaryFrequency[1/cm]  532.2373
WellDepth[kcal/mol]  34.3
WellDepth[kcal/mol] 11.3
End
Frequencies[1/cm]  65
                27.7948                  70.6610
  77.6506              136.2543              154.8382
 182.8958              239.8253              340.6894
 356.8632              409.6971              409.9841
 477.4442              485.2458              512.6473
 521.5793              535.5788              559.8827
 580.7187              633.6376              659.6130
 688.4179              696.3183              759.1767
 780.2217              782.3936              832.5819
 873.5417              878.7338              902.0204
 916.0132              964.9340              970.4237
 980.3804              996.9217             1042.1040
1141.4150             1171.4461             1174.5510
1179.7892             1229.6648             1273.2195
1288.7322             1369.7715             1393.8886
1401.8953             1416.5141             1421.1694
1465.1758             1497.2007             1538.4098
1604.4867             1639.6767             1666.9434
1997.4584             3087.3002             3157.8222
3162.1219             3164.2455             3175.2643
3177.4559             3188.0410             3189.1667
3246.8920             3249.0233             3436.0875
ZeroEnergy[kcal/mol]  -4.
ElectronicLevels[1/cm] 1
0  2
End
!-----------------------------------
End
```

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